TEXTILE RESEARCH JOURNAL

VOLUME XXIV November, 1954 NUMBER 11

PUBLICATION OF
TEXTILE RESEARCH INSTITUTE

Editorial Office: 10 East 40th Street, New York 16, N. Y.

TEXTILE RESEARCH JOURNAL

VOL. XXIV, No. 11 November, 1954

In This Issue

Cellulose Studies
Ludwig Rebenfeld and Eugene Pascu 941
Part XIX. Distribution of Methoxyl Groups in Partly Methylated Cellulose

A Microscopical Study of the Effects of Some Typical Chemical Environments on the Primary Wall of the Cotton Fiber
Verne W. Tripp, Anna T. Moore, and Mary L. Rollins 956

Fine Structure in Viscose Fibers
G. D. Joshi and J. M. Preston 971

Correction to August Issue 979

Abrasion Resistance of Multifilament and Staple Yarns Tested on Modified Walker Abrader
Edward Abrams and H. Paul Whitten 980

Quantitative Spectrographic Analyses of Metallic Elements in Textile Materials
Louis C. Block and David C. W. Kwok 990

LETTERS TO THE EDITOR
Micronaire-Fineness and Causticaire-Maturity Relationships 1000
The Nature of Fiber Friction 1002
An Orientation Concerning the Relations between Fiber and Yarn Properties in Several Mills 1003
The Dyeing of Cyanoethylated Cotton 1005

INDUSTRIAL SECTION
The Influence of Friction and Traveller Weight in Ring Spinning
J. Crank and Doreen D. Whitmore 1006
The Effect of Weathering in the Field on the Fiber Properties of Cotton
Lyle D. Hessler, Jack D. Towery, and Billy K. Power 1010

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TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Entered as second-class matter, April 27, 1945, at the post office at Lancaster, Pa., under the Act of August 24, 1912. Accepted for mailing at special rate of postage provided for in paragraph (d-2), Section 34.40, P. L. & R. of 1948, authorized May 9, 1950.

Manuscripts and communications should be sent to the editorial office, 10 East 40th Street, New York 16, N. Y.

Subscription rates: $15.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $1.50 each.

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TEXTILE RESEARCH JOURNAL

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Cellulose Studies

Part XIX. Distribution of Methoxyl Groups in Partly Methylated Celluloses*

Ludwig Rebenfeld† and Eugene Pacsu‡

Contribution from Textile Research Institute and Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Introduction

Although the partial methylation of cellulose was introduced by Denham and Woodhouse [6] in 1913, it was not until the last two decades that interest was aroused in the way that the methoxyl groups arrange themselves in the cellulose polymer.

If the degree of substitution (D.S.) is defined as the average number of substituents per anhydroglucose unit, then completely methylated cellulose would have D.S. = 3.0. The fact that such a product has never been obtained from native cellulose regardless of the method and number of methylations is considered by many workers as casting serious doubt on the classical structure of cellulose. By careful control of reagent concentration, reaction time and temperature, it is possible to obtain cellulose whose degree of substitution can vary from 0 to approximately 2.9. It is now realized that a methyl cellulose with a D.S. of 1.0, for example, does not consist of cellulose chains where every glucose monomer has one of the three available hydroxyl groups substituted by a methoxyl group; but, rather, along the cellulose chains one finds glucose units substituted in all three of the available positions, glucose units substituted in two of the available positions, monosubstituted glucose, and completely unsubstituted glucose units.

The statistical concept of a distribution of substituents was introduced by Spurlin [19], who in 1939 proposed that, if all the hydroxyl groups of cellulose have equal probabilities of reaction, then the substituents will arrange themselves along the cellulose polymer according to the laws of probability, and a statistical distribution of substituents will result. In order to make the necessary calculations to find such a theoretical distribution, Spurlin had to make the following assumptions: (*1*) cellulose is a sufficiently long chain of glucose units so that the end group may be neglected; (*2*) the ratio of the reactivities of the three hydroxyl groups is constant regardless of the average degree of substitution; (*3*) the reactivity of a hydroxyl group is not altered because of the previous methylation of another hydroxyl group in the same glucose unit; (*4*) certain ratios of rate constants of the three hydroxyl groups are assumed; and, finally, (*5*) all the hydroxyl groups of cellulose are available for reaction. Based on these assumptions Spurlin was able to construct curves indicating the amount of trimethyl glucose, dimethyl glucose, monomethyl glucose, and unsubstituted glucose which one should find at different degrees of sub-

* This article is based upon a dissertation submitted by Ludwig Rebenfeld in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. Previous papers in this series appeared in TEXTILE RESEARCH JOURNAL in 1945–1949 and in 1952.

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stitution. Until now very few attempts have been made to verify the Spurlin calculations, and those experiments that were performed were based on indirect methods of analysis or on inefficient vacuum distillation techniques.

In 1936 Traube [22] attempted a quantitative separation by vacuum distillation of the partly methylated methyl glucosides arising from the degradation of a partly methylated cellulose. Clear-cut separation was not obtained, but, making the assumption that each fraction contained only two constituents, Traube was able to calculate from the total weight of each fraction and the experimental methoxyl content of each fraction a distribution of trimethyl, dimethyl, monomethyl, and unsubstituted glucose. Although Traube's data cannot be used to prove or disprove the Spurlin assumptions, they did serve to show that substitution at least tends to be random since trimethyl glucose as well as unsubstituted glucose were found to be present in a methyl cellulose of D.S. approximately 1.5.

A somewhat similar approach to that of Traube was used by Compton [5] in 1938. He prepared the methyl glucosides of the acetolyzed water-soluble methyl cellulose, D.S. approximately 0.8, obtained by methylation of wood pulp and viscose rayon in dimethyldibenzylammonium hydroxide with dimethyl sulfate, and then fractionated by vacuum distillation the partly methylated and acetylated methyl glucosides. The conclusion was drawn, from the fractions of high and low methoxyl contents and from the isolation of certain crystalline compounds, that the methylation of cellulose dispersed in the quaternary ammonium base proceeds by diffusion of the methylating reagent into a particle structure, from which it follows that the cellulose is not molecularly dispersed. The method of separation used in this work suffers from the same drawback as that employed by Traube, since clear-cut separation of the partly methylated monomers is not possible by vacuum distillation.

In a series of researches on partly alkylated cellulose, Mahoney and Purves [13] determined the distribution of the remaining free hydroxyl groups by an indirect procedure. These investigators esterified the free hydroxyl groups with *p*-toluene sulfonyl chloride (tosyl chloride) and then preferentially replaced the primary tosyl groups with iodine by the use of sodium iodide in an acetone medium. From the experimentally determined sulfur and iodine contents they were able to deduce the number of free primary hydroxyl groups, *i.e.*, hydroxyls in position 6 of the glucose monomer. Further, by use of the lead tetraacetate and periodic acid oxidation techniques they were able to deduce the number of free hydroxyl groups in the 2 and 3 positions. As is clearly seen from the nature of these experimental reactions, the distribution data which were obtained by these workers are indirect and must therefore reflect the inaccuracies of all the reactions performed. Neither tosylation, iodide exchange of primary tosyl groups, periodate oxidation, nor lead tetraacetate oxidation can be considered to be stoichiometrically quantitative when applied to a polymeric system.

Timell [21] combined the techniques of Traube and Purves and fully characterized partly alkylated celluloses; however, his data suffer from the inaccuracies of the indirect method of Purves and of the incomplete separation by vacuum distillation of the Traube method.

No other attempt at determining the distribution of substituents is available in the literature. It is the purpose of this study to report the experimental distribution curves determined by a new analytical procedure.

It seems probable that different distributions of substituents will be obtained when the cellulose is methylated under different experimental conditions and when the cellulose is in different states of aggregation. Thus, methylation of solid, fibrous cotton cellulose with sodium hydroxide and dimethyl sulfate should not produce the same material resulting from methylation performed on cellulose dissolved in a suitable dispersing agent, where the methylation should be homogeneous. Bock [2] observed that a methylated product obtained homogeneously differs radically from a heterogeneously methylated product of the same average degree of substitution. He found that a homogeneously prepared methyl cellulose of D.S. 0.7 is soluble in cold water, while for a heterogeneously prepared methyl cellulose a D.S. of 1.2 is required before cold-water solubility is attained. Bock suggests that this difference can be ascribed to a different distribution of methoxyl groups, the homogeneously prepared product being more uniform.

In addition to methyl cellulose samples prepared in this laboratory, a commercial product, Methocel, was investigated as to its substituent distribution.

This material represents an example of heterogeneous methylation since solid cellulose impregnated with sodium hydroxide is the starting material used for its preparation. However, the active methylating agent is gaseous methyl chloride, and it was of interest to see the effect of an easily diffusible gaseous reagent on the distribution of the methoxyl groups.

Theoretical Distribution of Substituents

It is difficult to calculate the distribution of substituents in a polymer without making certain simplifying assumptions. Such a calculation for cellulose ethers was made originally by Spurlin [19] and later modified by Timell [21]. Spurlin postulated that substitution will take place along the polymer according to the laws of probability when all the hydroxyl groups of cellulose are available for reaction and when "the ratio of the reactivities of the three sorts of hydroxyl groups is independent of the degree of substitution of the cellulose chain as a whole." Both Spurlin and Timell constructed theoretical distribution curves, making these assumptions, and they based their calculation on first-order kinetics.

From a general knowledge of hydroxyl group reactivities in carbohydrate chemistry it is known that the rate constants for methylation of the three available hydroxyl groups in cellulose are not in the ratio of 1:1:1. The hydroxyl group in position 6 is a primary one and is therefore radically different from the two seconadry hydroxyl groups in positions 2 and 3. Even these two secondary hydroxyl groups differ in their reactivities because of their steric configuration as well as because of their relative proximity to the potential aldehyde group in position 1 of the anhydroglucose unit. Since the rate constants for methylation of the three hydroxyl groups are not known, it is only possible to assume certain values, or, more correctly, to assume certain ratios of the three reaction rate constants. A suitable ratio to assume is 5:1:10 for hydroxyls on carbons 3, 6, and 2, respectively, although it is evident that it is of no consequence which of the hydroxyl groups are assigned the larger values. Distribution curves for various ratios of rate constants were calculated by Spurlin and by Timell, and for the purpose of this research the curves arising from a ratio of 5:1:10 and 1:1:1 are considered. The theoretical curves obtained by these workers are reproduced in Figures 2 to 13.

When the ratio of the reactivities of the three types of hydroxyl groups is 1:1:1, a simpler calculation can be made, utilizing the concept of statistics. This method of calculation was proposed by Dr. James H. Wakelin of Textile Research Institute, and the authors are indebted to him for this contribution. If one imagines cellulose to be a series of n glucose units each of which possesses three available reaction positions, then random methylation can be considered as the process of attaching methoxyl groups on any of the $3n$ available positions. For the purpose of this calculation the degree of substitution (D.S.) must be redefined as the probability of finding any given three hydroxyl groups substituted by a methoxyl group. $P = \text{D.S.}/3$ is therefore the probability of finding any one particular hydroxyl group so substituted. Since the probability of three equal and consecutive events taking place is given by the cube of the probability of one such event occurring, then P^3 represents the probability of finding all three hydroxyl groups on one glucose unit substituted by a methoxyl group. In other words, P^3 represents the fraction of trimethyl glucose to be expected from a methyl cellulose of the particular degree of substitution under discussion; $(1 - P)$ is the probability of a hydroxyl group remaining unreacted, and therefore $(1 - P)^3$ is the fraction of unsubstituted glucose units to be expected. It is clear that P^3 and $(1 - P)^3$ are the first and last terms of the expansion of the binomial term $[(P) + (1 - P)]^3$. The second and third terms of such an expansion give the fraction of dimethyl glucose and monomethyl glucose, respectively, which are to be expected at a certain degree of substitution:

$$[(P) + (1 - P)]^3 = P^3 + 3P^2(1 - P) + 3P(1 - P)^2 + (1 - P)^3. \quad (1)$$

By inserting values of P from 0 to 1 into the above expression, it is a simple matter to calculate theoretical distribution curves. It is imperative to remember the underlying assumptions that all the hydroxyl groups are available for methylation and that the ratio of the reaction rate constants of hydroxyl groups on carbons 2, 3, and 6 is 1:1:1, and, further, that this ratio does not change as the degree of substitution increases from 0 to 3.

Experimental Procedure

Preparation of Methyl Cellulose

Raw-material preparation.—For the homogeneous methylation a hydroviscose cellulosic material was

used which was prepared in the following manner: American Viscose Corp. Crown Rayon 40-filament, 150-den. viscose yarn was scoured for 1 hr. with a 2% neutral soap solution at 60°C, rinsed thoroughly with tap water, and finally washed with distilled water and dried at 55°C. Ten grams of this material was then hydrolyzed in 250 ml. of 1*N* hydrochloric acid for 20 hrs. at 60°C. After the required hydrolysis time, the hydroviscose was washed free of hydrochloric acid and dried in an oven at 55°C. The degree of polymerization was determined by measuring the intrinsic viscosity of this product dissolved in cuprammonium hydroxide. This method was discussed by Mehta and Pacsu [14]; a value of 51 glucose units was obtained, which corresponds closely to the cellulosic product described as limit hydroviscose by these workers.

For the heterogeneous methylation a carded cotton sliver was used. It was purified by a 6-hr. Soxhlet extraction with acetone followed by a 6-hr. extraction with benzene. After complete drying the cotton was boiled for 6 hrs. in a 2% sodium hydroxide solution under an atmosphere of nitrogen and thoroughly washed successively with tap water, distilled water, and methyl alcohol, and was finally dried at 55°C. This is a standard purification procedure used in Textile Research Institute laboratories, and yields a pure cellulosic material with a minimum of degradation. The degree of polymerization of this product was determined by the viscosimetric technique, and a value of approximately 3000 was obtained.

Homogeneous methylation.—Hydroviscose forms an optically clear dispersion in certain quaternary ammonium hydroxides. Brownsett and Clibbens [3] have presented solubility data of cellulosic materials as a function of molecular weight and normality of the dispersing agent. They found that cellulose of low degree of polymerization, such as hydroviscose, dissolves completely in a 2.2*N* aqueous solution of trimethylbenzylammonium hydroxide, commercially known as Triton B. The homogeneous methylation procedure followed in the present work was essentially that described by Bock [2] and Johnston [10], although the method of recovery of the methylated product has been substantially altered. A 2% to 5% solution of hydroviscose in this solvent is readily obtained in about 30 min. with stirring and cooling to about 5°C, which enhances the swelling and solvating effect of the solvent on the hydroviscose. Dimethyl sulfate is added to this solution, with stirring, in varying amounts depending on the desired degree of substitution, and the reaction is allowed to proceed for several hours at 5°C. Evidently this procedure is highly empirical, and it is only by repeated experiments and continued variation of such parameters as cellulose concentration, dimethyl sulfate concentration, and time of reaction that it is possible to obtain a product of desired degree of substitution.

At the end of the reaction period the excess trimethylbenzylammonium hydroxide is neutralized with sulfuric acid, and all inorganic ions are dialyzed out in a cellophane dialysis tube against distilled water during a period of about 3 days. At this point a fraction of the methyl cellulose precipitates in the dialysis tube, and this is separated by centrifugation, washed with distilled water and acetone, and dried in a vacuum oven at 80°C. This material, designated as fraction *A*, is generally of low degree of substitution since it is insoluble in cold water. The mother liquor and the washings from this first fraction are combined and evaporated under reduced pressure at approximately 45°C to a volume of not more than 10 ml., and the methyl cellulose is then precipitated from this viscous, concentrated solution by the addition of a large volume of acetone. Centrifuging, washing with acetone, and drying *in vacuo* at 80°C yields the remainder of the methyl cellulose, which is designated as fraction *B*. Generally this material has a high degree of substitution, and the sum weight of fraction *A* and fraction *B* usually constitutes a 90% recovery on the basis of the starting material. The loss at this point can be ascribed to incomplete precipitation of fraction *B*, passage of low degree of polymerization material through the dialysis membrane, and unavoidable mechanical loss. The methyl cellulose products obtained by this procedure are generally white amorphous powders, although occasional samples are slightly brown because of occluded impurities which were not removed during the dialysis procedure. Such samples still yield valid distributional data, but the experimentally determined methoxyl contents will be in error.

Heterogeneous methylation.—The method used for heterogeneous methylation was that described by Steele and Pacsu [20] and was varied only in the attempt to obtain low as well as high degree of substitution.

Ten grams of the previously described purified native cotton cellulose is flushed through with oxygen-free nitrogen for 1 hr. to remove entrapped

air which in the presence of concentrated sodium hydroxide would cause extensive oxidative degradation of the cellulose. This material is then steeped for 45 min. in 40% (weight %) sodium hydroxide solution also previously flushed with nitrogen, and the entire system is kept under an atmosphere of nitrogen. After half of the impregnation time, the sodium hydroxide solution is decanted and a fresh portion of alkali is added. The alkali cellulose is then pressed out thoroughly to remove excess sodium hydroxide solution, and the material is steeped in about 300 ml. of toluene to which 50 ml. of dimethyl sulfate has been added. The toluene serves both to dilute the methylating agent and thus prevent the vigorous exothermic hydrolysis reaction as well as to provide an inert oxygen-free atmosphere. The reaction is allowed to proceed for about 8 hrs., and one such methylation will result in a product of approximate D.S. 1.5. In order to obtain products of lower degree of substitution a smaller quantity of dimethyl sulfate as well as a shorter reaction time must be used. For the preparation of a more highly substituted methyl cellulose, the methylation procedure must be repeated. The product from the first cycle is filtered, washed thoroughly with boiling distilled water, and, without drying the product, the methylation is repeated. After five to eight such methylation cycles a product is obtained whose average degree of substitution is about 2.8. Further methylation cycles do not result in any appreciable increase in methoxyl content. After the final methylation and washing steps the product is dried in a vacuum oven at 80°C. Nearly quantitative yields are obtained in all such methylations, and, by control of the parameters such as dimethyl sulfate concentration, time of reaction, and number of methylation cycles, it is possible to obtain products whose degree of substitution varies from 0.3 to 2.8. Although a methyl cellulose obtained by this procedure is not visibly different from the starting cotton cellulose, the fibers have substantially lost their tensile strength. This is particularly true of samples with a high degree of substitution.

Commercial methylation.—The commercial methyl cellulose samples, Methocel,* were obtained whose average degree of substitution varied from 0.2 to 2.9 and represented products of a heterogeneous gaseous methylation. Although the exact manufacturing procedure is not available, the essential step seems to consist of treating alkali cellulose with methyl chloride under pressure. The products are white powders which at suitable degree of substitution are soluble in cold water and can therefore be used commercially as sizes and temporary textile finishing agents.

Methoxyl analysis.—The methoxyl analyses were performed according to the volumetric procedure proposed by Vieböck and Schwappach [23], modified by Clark [4], and further modified by Steele and Pacsu [20]. Completely dried and accurately weighed 5- to 10-mg. samples of the product to be analyzed are hydrolyzed with constant-boiling hydriodic acid at the boil for 40 min. The methyl iodide liberated during the hydrolysis is trapped in receiving tubes containing free bromine in a 10% solution of potassium acetate in glacial acetic acid. A reaction between methyl iodide and bromine ensues, giving rise to iodomonobromide, which, upon the addition of water and a 25% aqueous sodium acetate buffer, forms an amount of iodic acid equivalent to the methyl iodide, which in turn is equivalent to the methoxyl groups present in the product under analysis. The iodic acid can now be determined in the usual manner by titration of free iodine liberated from potassium iodide with standard sodium thiosulfate solution to a starch end-point. This allows the calculation of the % methoxyl content, which can then be converted to the average degree of substitution by the relation

$$\text{D.S.} = \frac{1.62F}{31 - 0.14F},$$

where D.S. = degree of substitution and F = percent methoxyl content.

Chromatographic Analysis

Hydrolysis of sample.—The following was adopted as the standard hydrolysis procedure for all the methyl cellulose samples regardless of their degree of polymerization or substitution. Essentially it is the method of Monier-Williams [15], who used it to obtain a nearly quantitative yield of glucose from native cotton cellulose. One hundred milligrams of the sample under analysis is dissolved in 3 g. of 72% (weight %) sulfuric acid and allowed to stand at room temperature for at least 15 hrs., generally overnight. Materials of high D.P. and low D.S. are more difficult to dissolve than those of low D.P. and high D.S., but in all cases complete solution is obtained after stirring for about 2 hrs. After the initial hydrolysis period, the solution is diluted with water until it is 1N with respect to sulfuric acid and is

* Supplied through the courtesy of Mr. Kenneth Bacon of the Dow Chemical Co. of Midland, Mich.

hydrolyzed on a boiling-water bath for 4 hrs. under reflux. The solution is then neutralized by passage through a weakly basic anion-exchange resin, Amberlite IR 4-B,* and the sugars are washed from the resin with approximately 400 ml. of distilled water. Concentration of the column eluate by evaporation under reduced pressure at temperatures not exceeding 50°C results in a sirup consisting of a mixture of partly methylated glucose units which are now ready for chromatographic analysis.

Qualitative paper partition chromatography.—Paper partition chromatography is now an accepted tool for the separation of a mixture of closely related substances in both the inorganic and organic fields, and its application to carbohydrate chemistry is well described by Wolfrom and Binkley [24]. The paper used in these experiments is Whatman Filter Paper No. 1, and it is cut into strips 22 in. in length and 6 in. in width. A starting line is drawn 3 in. from one end of the long dimension, and a drop of the hydrolyzate is applied to this starting line by use of a finely drawn-out capillary tube. Repeated superimposed application of the hydrolyzate is made while drying the spot between each application with a stream of hot air. When a sufficient amount of sugars has been applied, generally 1 mg., descending paper partition chromatography is then allowed to proceed, using a 10% undersaturated Partridge [17] solvent as the eluting agent. Such a solvent is prepared by adding *n*-butanol to the separated top butanol-rich layer of a mixture of 5 parts water, 4 parts *n*-butanol, and 1 part ethanol. When the solvent front has migrated to the bottom of the paper, the chromatogram is removed from the chamber and allowed to dry in air. The paper is then sprayed with a solution of aniline hydrogen phthalate [18] in water-saturated *n*-butanol, and the chromatogram is heated in an oven at 110°C for 7 to 10 min. to develop the spots. A sample which contains all four possible constituents, *i.e.*, glucose, monomethyl, dimethyl, and trimethyl glucose, will have four spots at approximate R_f values of 0.15, 0.30, 0.55, and 0.73, respectively. The R_f value is defined as the ratio of the distance of migration of a particular substance to the distance of migration of the solvent front. Although the R_f value is a variable quantity, being dependent on temperature and exact solvent composition, it is quite useful in a general qualitative identification. Thus, for example, on the basis of R_f values it is possible to distinguish between a monomethyl glucose and a dimethyl glucose, but it is generally not possible to distinguish between the various isomers of monomethyl glucose or between those of dimethyl glucose.

The four spots on our chromatograms were proved to be glucose, monomethyl, dimethyl, and trimethyl glucose both by the R_f value technique and by running alongside the unknown hydrolyzate a series of known methylated sugars. It is very interesting to note that in all the chromatograms prepared in this work no spot corresponding to tetramethyl glucose was observed. This substance would appear below the trimethyl glucose spot, and its presence would be expected from highly methylated cellulose on the basis of the classical structure. This absence of tetramethyl glucose, especially from materials of very low degree of polymerization, constitutes one of the major unsolved problems in cellulose chemistry.

Quantitative paper partition chromatography.—A general method for quantitative paper partition chromatography consists of eluting the material to be analyzed from the chromatogram with a suitable solvent. In the case of sugars, water is most commonly used. In such a method, paper partition chromatography is merely employed as a means of separation while standard analytical procedures must then be applied for the quantitative determination. This method was introduced into the field of carbohydrate chemistry by Hirst, Hough, and Jones [9] and with slight procedural modification is the technique adapted in this research.

The same type and size of paper is used as in the qualitative procedure, but the unknown hydrolyzate is applied to the paper in a different manner. The starting line is marked off approximately 1 in. from each end of the short dimension, and these side strips are referred to as "location guides." The hydrolyzate is applied to the two location guides on the starting line and also in the form of a band to the major center portion of the chromatogram. The chromatogram is run in the usual manner, and, after drying, the location guides are cut off from the two edges of the paper. The location guides are then sprayed with aniline hydrogen phthalate in order to develop the spots corresponding to the methylated sugars. Placement of the location guides along the major portion of the chromatogram serves to locate the position of the sugars on the central undeveloped part of the paper, and the strips of paper containing the

* Manufactured by Rohm & Haas Co., Philadelphia, Pa.

individual sugars can be cut from the paper with a pair of scissors.

The method used for eluting the sugars from the paper strips was described by Dimler et al. [7] and is only slightly modified in this work. The strips of paper containing the various separated sugars are clamped between two microscope slides. The major portion of the paper hangs over the edge of the slides, and the free ends of the glass slides are dipped into a watch glass containing pure water. By means of capillary action the sugars are eluted from the paper and allowed to drip into a receiving flask. Usually about 10 ml of water are collected to insure complete elution of the sugars from the paper strips, although virtually all the sugar comes over with the first two or three drops. At this point one has the glucose, monomethyl, dimethyl, and trimethyl glucose in pure form in four separate flasks, and it then remains to determine the concentrations of these four solutions. Clearly such a method of separation is more efficient than the vacuum distillation technique used by Traube since no overlapping takes place here.

Standardization of titrations.—Although the separation of the four sugars by paper chromatography yields these sugars in pure form, in order to obtain proper distribution data it is imperative that the analytical procedure be reliable. The method to be used here must be both accurate and rapid since a large number of such samples must be determined. As is obvious from the nature of paper partition chromatography, one deals here with very small amounts of material, and the analytical procedure must be suitable in the semimicro range. In these experiments the amount of sugar mixture applied to the chromatogram ranged from 15 to 25 mg., and, if one considers that one of the constituents may be a minor one, for example 1%, the problem then resolves itself into finding a suitable means for determining reducing sugars in the range of 0.20 to 10.0 mg.

Several methods are available for the determination of glucose and methylated derivatives of glucose; however, not many of these can be applied with any reasonable accuracy in the semimicro range. Blom and Rosted [1] gave a comprehensive review of the methods used in determining reducing sugars by the use of oxidizing agents, and generally concluded that a properly standardized procedure utilizing free iodine in an alkaline buffer gives reliable results.

Lippoid [12] investigated the use of this method for the range of 1 to 85 mg. and found that reliable results can be obtained provided that a standardized procedure is followed. It was necessary to extend the lower range of this procedure to 0.20 mg. of sugar and to establish the optimum conditions for such an analytical procedure. In order to accomplish this, known solutions containing 1 mg. of glucose were determined, and the following experimental procedure was established. To the sugar in approximately 30 ml. of water are added 2 ml. of 0.05*N* iodine solution, followed by 1 ml. of a standard buffer solution at pH 10.2 which is 0.4*M* in sodium carbonate and 0.1*M* in sodium bicarbonate. The reaction is allowed to proceed in the dark for 2 hrs., after which the solution is acidified with 10 ml. of 2*N* sulfuric acid. The liberated iodine is then back-titrated with a standard 0.01*N* sodium thiosulfate solution to the disappearance of the blue iodoamylose complex. A correction must be made for the reagents as well as for the blank paper used in the chromatography, and this value must be subtracted from the actual determination.

By use of this procedure it is possible to determine glucose in the range of 0.2 to 4.0 mg., as can be seen from the following data:

Glucose taken (mg.)	Glucose found (mg.)
0.21	0.22
0.31	0.33
0.52	0.52
0.82	0.81
1.03	1.05
2.06	2.05
2.58	2.57
3.09	3.10
4.01	4.03

When larger amounts of sugar are to be determined it is necessary to increase the amount of iodine; however, it is imperative that the amount of buffer be increased proportionately since the ratio of iodine to buffer must remain constant. It is interesting to note the effect of both the iodine concentration and the buffer concentration on the accuracy of the method (Figure 1).

Identification of isomers.—As stated previously, it is not possible by one-dimensional chromatography to distinguish among the three possible isomers of monomethyl glucose or among those of dimethyl glucose. Recently Lemieux and Bauer [11] described a procedure whereby the monomethyl glucose isomers can be identified by paper partition chromatography, and this method was applied to the mono-

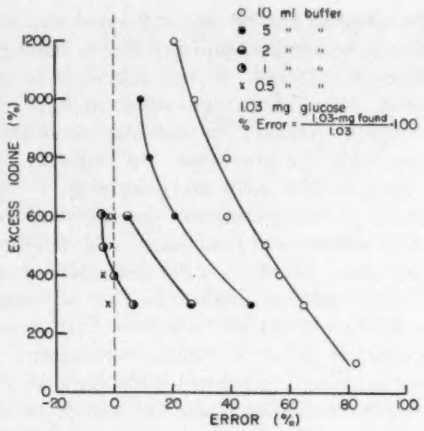

FIG. 1. *Dependence of error on buffer and iodine concentrations in the determination of glucose.*

methyl glucose fraction of the hydrolyzed methyl cellulose, with the following result. All the methyl celluloses, regardless of their degree of substitution or method of preparation, showed the presence of 2-monomethyl and 3-monomethyl glucose, but no evidence was found for the presence of the 6-monomethyl glucose isomer.

Inspection of structural formulas of the three possible dimethyl glucose isomers suggested that one might be able to distinguish such isomers by an extension of the Lemieux and Bauer technique. When the method was applied to the dimethyl glucose fraction, it was found that the dimethyl glucose isomers were the same regardless of the method of preparation or of the degree of substitution of the methyl cellulose. The presence of 2,6-dimethyl glucose and 2,3-dimethyl glucose was established; however, no 3,6-dimethyl glucose isomer was observed.

Experimental Distribution of Substituents

Homogeneous Methylation

In order to obtain data for the determination of experimental distribution curves for homogeneously methylated cellulose, a series of hydroviscose samples was methylated by the procedure outlined in the experimental section. Samples with degree of substitution ranging from 0.33 to 2.19 were prepared by control of reagent concentrations and reaction time. It is not possible to obtain homogeneously prepared products with degree of substitution higher than 2.2 since above this value the material is considerably hydrophobic and precipitates from the reaction mixture. Any further methylation of the precipitated material would not be of a homogeneous nature but would assume the characteristics of a heterogeneous reaction. Generally products with a low degree of substitution are designated fraction *A, i.e.*, materials insoluble in cold water which precipitated upon dialysis of the neutralized reaction mixture; while the high degree of substitution products are fraction *B,* those obtained from the aqueous solution by acetone precipitation. Since the actual methylation of both these fractions is homogeneous, no differentiation was made in the tabulation of the experimental data.

Triplicate analyses were performed after hydrolysis and quantitative paper-partition chromatography of the samples. The reproducibility and accuracy of the analytical procedures are illustrated in Table I, where the individual analyses of the triplicates are given for one sample. Comparable accuracy was attained in all other samples.

It should be noted that an additional check on the analytical procedures can be obtained in the following manner. The degree of substitution of the methylated cellulose is determined by a direct methoxyl analysis in the usual way. The average degree of substitution of the sugar mixture resulting from the hydrolysis of the methyl cellulose can then be calculated from the distribution data obtained by the chromatographic technique. The two values for the degree of substitution, which are obtained by independent means, should agree, and it is then logical to conclude that all the analytical procedures are correct and one can have complete confidence in the experimental distributions. Such agreement was obtained for most samples; where agreement was not satisfactory the degree of substitution value obtained by quantitative paper partition chromatography was taken as the correct value and the discrepancy ascribed to the presence of occluded inorganic impurities.

TABLE I. HOMOGENEOUS METHYLATION (DEGREE OF SUBSTITUTION 0.92) DATA SHOWING ACCURACY OF ANALYTICAL PROCEDURES

Chromatogram	Experimental distribution (%) *I*	*II*	*III*	Ave.	Theoretical distribution* (%)
Glucose	34.9	34.1	34.1	34.4	33.1
Monomethyl glucose	39.7	39.2	39.4	39.4	44.3
Dimethyl glucose	20.1	20.4	20.5	20.3	19.7
Trimethyl glucose	5.3	6.3	6.0	5.9	2.9

* 1:1:1 ratio of rate constants, eq. (1).

In Table II are presented the average experimental distribution data for homogeneously prepared methyl celluloses in Triton B solution. The experimental distribution data as well as the theoretical distribution data assuming the ratio of rate constants to be 1:1:1 and 5:1:10 [19, 21] are plotted in Figures 2 to 5.

Heterogeneous Methylation

Experimental distribution curves for heterogeneously methylated cellulose were obtained by analyzing products whose degree of substitution ranged from 0.30 to 2.75. These materials were prepared by the procedure previously described, and the distribution of substituents was determined by the quantitative paper partition chromatography technique. The average of triplicate analyses is summarized in Table III, and the experimental as well as theoretical distribution curves are plotted in Figures 6 to 9. It will be noted in Table III that the sample of 1.64 D.S. differs considerably from the sample of 1.57 D.S. This arises from a slight modification in the procedure used in the preparation of the 1.64 D.S. sample. A wetting agent, Alkonol WXN, was incorporated in the sodium hydroxide solution. The striking effect that a wetting agent exerts on the manner of distribution of the methoxyl groups will be discussed later.

Commercial Methylation

The data used for the construction of the experimental distribution curves for commercial methyl celluloses are presented in Table IV and are plotted in Figures 10 to 13 along with the theoretical distributions. The products which were analyzed varied in the degree of substitution from 0.24 to 2.46, and triplicate analyses were performed for each sample.

TABLE II. EXPERIMENTAL DISTRIBUTION OF METHOXYL GROUPS IN HOMOGENEOUSLY PREPARED METHYL CELLULOSE

Degree of substitution (D.S.)	Glucose (%)		Monomethyl glucose (%)		Dimethyl glucose (%)		Trimethyl glucose (%)	
	expt.*	theor.†	expt.*	theor.†	expt.*	theor.†	expt.*	theor.†
0.33	73.1	70.5	19.1	26.2	5.7	3.2	2.1	0.1
0.47	66.2	59.9	19.8	33.5	9.2	6.2	4.8	0.4
0.57	59.4	53.1	24.2	37.4	11.0	8.8	5.5	0.7
0.63	57.6	49.3	23.2	39.3	11.2	10.5	8.0	0.9
0.92	34.4	33.1	39.4	44.3	20.3	19.7	5.9	2.9
1.24	22.6	20.5	35.9	42.8	29.7	29.8	11.8	6.9
1.72	10.8	8.0	25.7	31.6	38.0	41.9	25.5	18.5
1.78	7.8	6.7	26.9	29.5	39.6	42.9	25.7	20.9
1.84	6.8	5.8	25.0	27.6	39.8	43.6	28.4	23.0
1.98	4.7	3.9	20.4	22.9	40.8	44.4	34.1	28.8
2.19	2.5	2.0	15.3	16.0	39.4	43.1	42.7	38.9

* Average of three analyses.
† Theoretical value assuming the ratio of rate constants to be 1:1:1, equation (1).

TABLE III. EXPERIMENTAL DISTRIBUTION OF METHOXYL GROUPS IN HETEROGENEOUSLY PREPARED METHYL CELLULOSE

Degree of substitution (D.S.)	Glucose (%)		Monomethyl glucose (%)		Dimethyl glucose (%)		Trimethyl glucose (%)	
	expt.*	theor.†	expt.*	theor.†	expt.*	theor.†	expt.*	theor.†
0.30	78.9	72.9	10.6	24.3	3.9	2.7	6.6	0.1
0.71	66.1	44.2	6.2	41.5	7.9	13.0	19.8	1.3
1.37	40.7	16.0	8.2	40.4	11.8	34.0	39.2	9.6
1.57	36.5	11.1	6.8	35.9	13.0	38.9	43.8	14.1
1.85	19.8	5.7	13.5	27.2	19.0	43.7	47.8	23.4
2.47	3.5	0.6	6.3	8.0	24.3	36.3	65.9	55.1
2.74	1.7	0.1	2.0	2.0	15.0	22.2	81.5	76.1
1.64‡	17.9	9.1	21.0	33.4	31.6	40.9	29.5	16.6

* Average of three analyses.
† Theoretical value assuming the ratio of rate constants to be 1:1:1, equation (1).
‡ Methylated in the presence of wetting agent.

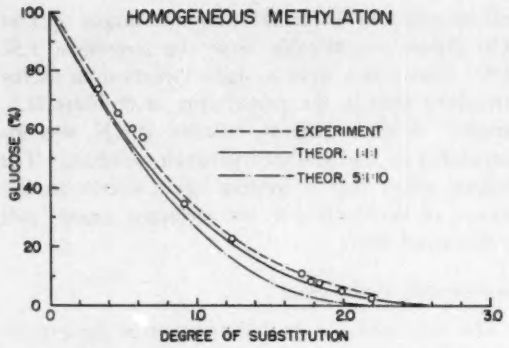

FIG. 2. *% Glucose vs. degree of substitution in homogeneously methylated cellulose.*

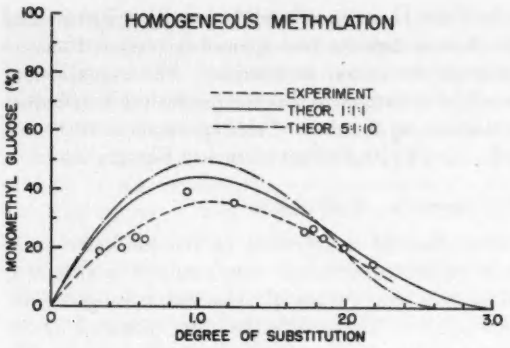

FIG. 3. *% Monomethyl glucose vs. degree of substitution in homogeneously methylated cellulose.*

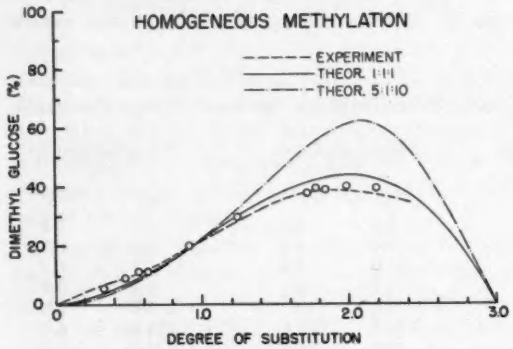

FIG. 4. *% Dimethyl glucose vs. degree of substitution in homogeneously methylated cellulose.*

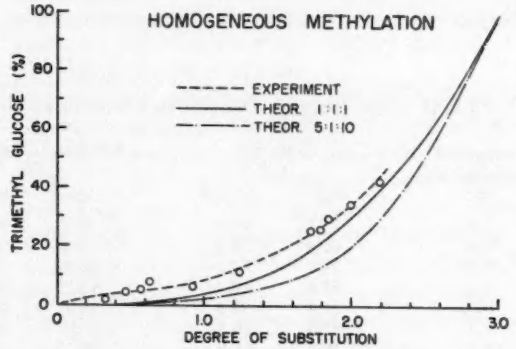

FIG. 5. *% Trimethyl glucose vs. degree of substitution in homogeneously methylated cellulose.*

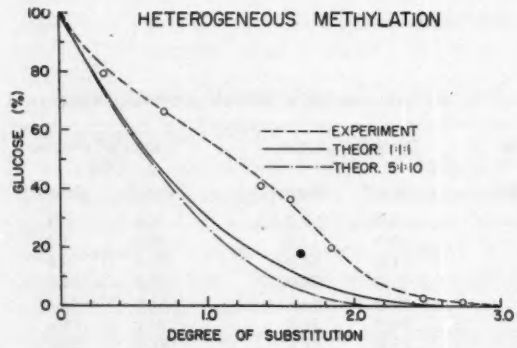

FIG. 6. *% Glucose vs. degree of substitution in heterogeneously methylated cellulose.* ○*—Normal heterogeneous methylation.* ●*—Heterogeneous methylation in the presence of wetting agent.*

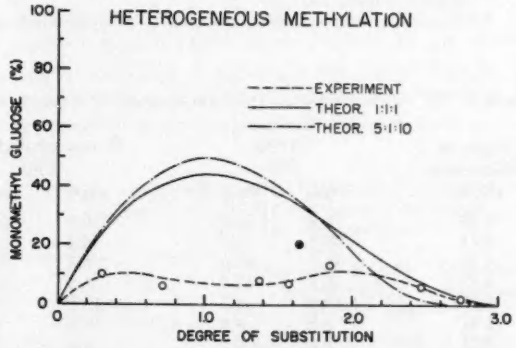

FIG. 7. *% Monomethyl glucose vs. degree of substitution in heterogeneously methylated cellulose.* ○*—Normal heterogeneous methylation.* ●*—Heterogeneous methylation in the presence of wetting agent.*

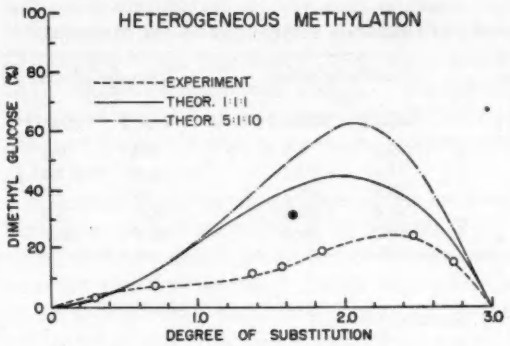

FIG. 8. *% Dimethyl glucose* vs. *degree of substitution in heterogeneously methylated cellulose.* ○—*Normal heterogeneous methylation.* ●—*Heterogeneous methylation in the presence of wetting agent.*

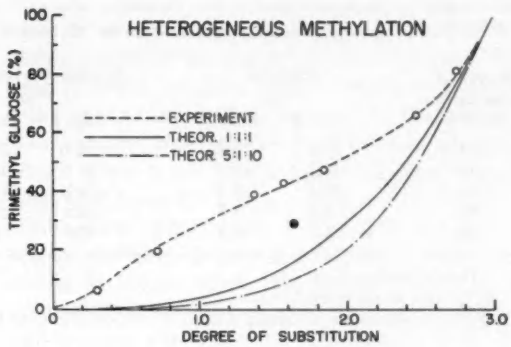

FIG. 9. *% Trimethyl glucose* vs. *degree of substitution in heterogeneously methylated cellulose.* ○—*Normal heterogeneous methylation.* ●—*Heterogeneous methylation in the presence of wetting agent.*

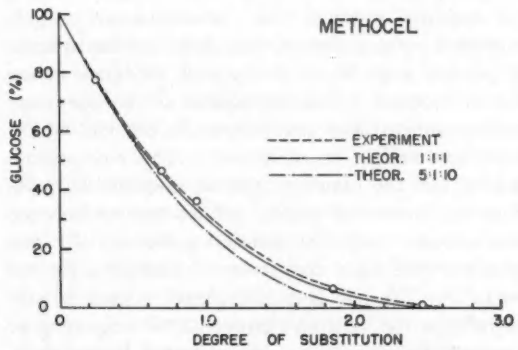

FIG. 10. *% Glucose* vs. *degree of substitution in commercial methyl cellulose, Methocel.*

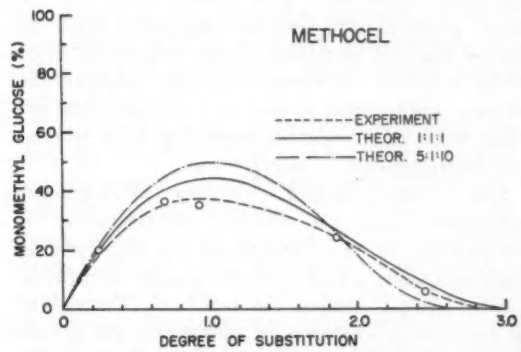

FIG. 11. *% Monomethyl glucose* vs. *degree of substitution in commercial methyl cellulose, Methocel.*

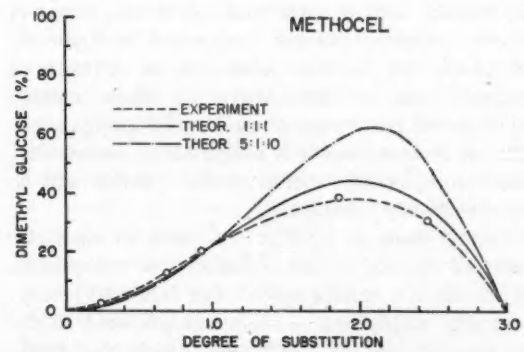

FIG. 12. *% Dimethyl glucose* vs. *degree of substitution in commercial methyl cellulose, Methocel.*

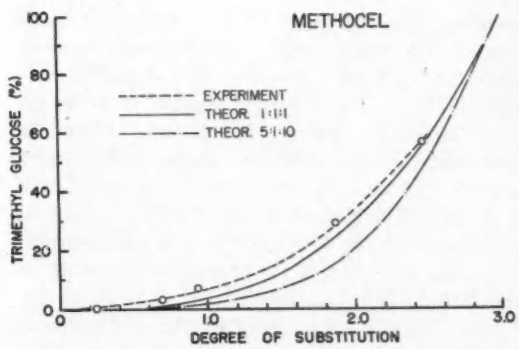

FIG. 13. *% Trimethyl glucose* vs. *degree of substitution in commercial methyl cellulose, Methocel.*

TABLE IV. EXPERIMENTAL DISTRIBUTION OF METHOXYL GROUPS IN COMMERCIAL METHYL CELLULOSE, METHOCEL *

Degree of substitution (D.S.)	Glucose (%)		Monomethyl glucose (%)		Dimethyl glucose (%)		Trimethyl glucose (%)	
	expt.†	theor.‡	expt.†	theor.‡	expt.†	theor.‡	expt.†	theor.‡
0.24	77.4	77.8	19.9	20.3	2.2	1.8	0.5	0.1
0.69	46.7	45.7	36.7	40.9	13.0	12.2	3.6	1.2
0.93	36.2	32.8	35.7	44.3	20.7	19.9	7.4	3.0
1.86	6.8	5.5	24.5	26.9	38.9	43.8	29.7	23.8
2.46	1.2	0.6	6.0	8.0	36.1	36.3	56.8	55.1

* Dow Chemical Co.
† Average of three analyses.
‡ Theoretical value assuming a ratio of rate constants to be 1:1:1, equation (1).

Discussion

Critical examination of the experimental distribution curves obtained in this work and comparison of these curves with the theoretical distribution curves affords an insight into the mechanism of the cellulose methylation reaction. It is quite evident that different products are obtained, depending upon the method that had been used for the preparation of the methyl cellulose. It seems reasonable, therefore, that different mechanisms should be assigned to the cellulose methylation reaction, depending upon whether it is heterogeneous or homogeneous.

The results obtained from the heterogeneous methylation allow the simplest interpretation. In this case the methoxyl groups are not distributed at random; rather, a very clear-cut course of methylation is followed during the reaction. Throughout the entire range of degree of substitution the amount of trimethyl glucose and unsubstituted glucose is much larger than is to be expected on the basis of a random or statistical distribution of methoxyl groups. For example, at D.S. 1.0 where a random distribution calls for 25% to 30% unsubstituted glucose depending upon the ratio of rate constants that is assumed, the experimental curve indicates approximately 55% glucose. For the same degree of substitution 2% to 4% trimethyl glucose is to be expected from a random distribution, while the experimental curve indicates approximately 30% trimethyl glucose. By the same token, only about 7% monomethyl glucose is found where a random distribution calls for 44% to 50% of monosubstituted units. The same is true for dimethyl glucose where from 22% to 24% is expected but only about 8% is found. These large discrepancies from a statistical distribution of the methoxyl groups are interpreted to indicate that the heterogeneous methylation is an excellent example of a topochemical reaction where the surface of the cellulosic substrate is first reacted upon. This initial reaction causes the formation of a predominantly trisubstituted fiber surface and an almost completely unsubstituted inner core. As the methylation is continued the reactants must diffuse through the hydrophobic outside layer into the inner portion of the fibers to allow further methylation of the hydroxyl groups. Such a mechanism, largely dependent upon diffusion, will cause the methylation to proceed from layer to layer at all times giving rise to products where the insides of the fibers are mainly unmethylated and where the outsides of the fibers are mainly trisubstituted. The monomethyl glucose and the dimethyl glucose undoubtedly arise from the somewhat poorly defined border between unsubstituted and trisubstituted polymer. At this portion of the fiber, conversion of another layer has begun but has not been completed. Since a vast majority of the hydroxyl groups at the beginning of the methylation reaction are protected from substitution by virtue of their position inside the fiber, a statistical distribution of substituents cannot be expected to take place.

The micellar cellulose structure is such that it can be swollen with suitable hydrophilic reagents. A swollen cellulosic material, because of its larger dimensions, will facilitate penetration or diffusion of reactants into the inner core. In effect, suitable swelling will make more of the hyroxyl groups available for reaction, and it is reasonable to assume that under such swollen conditions the cellulose will be more randomly substituted.

In this work an attempt was made to show the effect of swelling on the distribution of substituents by the use of a wetting agent. The D.S. 1.64 heterogeneously methylated product was prepared in the presence of Alkonol WXN, and indeed the distributional data obtained from this product are radically different from those found for the rest of the heterogeneously prepared methyl celluloses. The distri-

bution of substituents in this case is much more random and, as is seen from the solid points in Figures 6 to 9, the experimental data lie much closer to the theoretical distribution curves. This indicates that more hydroxyl groups were available for reaction, and this is undoubtedly due to the swelling effect of the wetting agent.

Examination of the distribution curves for homogeneously methylated cellulose in Figures 2 to 5 clearly indicates that a product of a different nature is under consideration here. Fairly close adherence of the experimental distribution data to the theoretical curves is observed, and it might be surmised at first that all the assumptions which were made in order to calculate the theoretical distribution curves have been fulfilled. Undoubtedly the most important assumption is the one that states that all the hydroxyl groups are available for reaction. The validity of this assumption is suggested by the nature of a homogeneous reaction. Dissolution of cellulose in a suitable solvent, a quaternary ammonium hydroxide solution in this case, will make all hydroxyl groups available for reaction provided that a true molecular solution of the cellulose is obtained. If the particles in the solution are molecules of cellulose, that is, chains of anhydro-β-glucose units, then the solution can be considered to be a molecular one. During the methylation of a molecular solution of cellulose it is indeed proper to expect that the substituents will distribute themselves according to the laws of probability. A cursory examination of the experimental distribution curves suggests that the distribution of substituents is indeed random, and one might therefore conclude that the solution is molecular.

When the experimental curves are examined critically, one observes that there is an unmistakable deviation from the theoretical curves. In addition to the fact that such a deviation exists, it is important to note the direction of deviation. For the purpose of this discussion only the trimethyl glucose curve (Figure 5) will be examined, but the same considerations apply to the other units as well. For every methyl cellulose sample analyzed, the amount of trimethyl glucose is higher than is to be expected from the theoretical distribution curve, where a ratio of rate constants of 1 : 1 : 1 is assumed. At this point it is important to ascribe to the 1 : 1 : 1 theoretical distribution curve a greater significance than has been done so far. If substitution is assumed to take place according to the laws of probability and if all hydroxyl groups are available, then the highest amount of trimethyl glucose will be obtained when the rate constants for methylation are equal. Any ratio of the rate constants other than 1 : 1 : 1 will predict a smaller amount of trimethyl glucose. The most favorable condition under which a fully substituted glucose unit will form is where the rate constants for the three hydroxyl groups are equal and where there is no preferential methylation of any particular hydroxyl group. The theoretical distribution curve based on the 1 : 1 : 1 ratio of rate constants, therefore, represents the upper limit of a family of curves which can be constructed by assuming different ratios of rate constants. Since the experimental curve lies above this upper limit, it is evident that the deviation must be explained by some means other than assuming different ratios of rate constants. This deviation is most significant in samples of low degree of substitution where, for example, at D.S. 0.33, 0.1% trimethyl glucose is to be expected and 2% is actually found. This large deviation becomes even more significant when it is considered that 0.1% represents an impossible upper value since the ratio of the rate constants is certainly not 1 : 1 : 1.

If the cellulose were not dispersed molecularly, then all of the hydroxyl groups would not be available for methylation. Such a condition would exist if the cellulose solution were micellar, where a micelle is considered to be an aggregate of cellulose molecules. Such a micelle would possess an inner portion less accessible than the micellar surface. Methylation would then be preferential on the surface of such a micelle, giving rise to a larger amount of trimethyl glucose than would be expected from a molecular solution where no such surface exists. This condition approximates that in the heterogeneous reaction, although the degree of heterogeneity is by orders of magnitude less during the homogeneous methylation. The fact that homogeneous methylation does not yield a distribution of methoxyl groups in accordance with a theoretical distribution of methoxyl groups strongly suggests that the solution of cellulose in trimethylbenzylammonium hydroxide is micellar and not molecular in nature.

It is important to note at this point that there may be no difference between a micellar and a molecular solution of cellulose. This would be so if a micelle of cellulose were in fact a molecule of cellulose. Obviously a micelle must be held together by some intermolecular forces. It is not likely that these are hydrogen bonds since these would not be expected to survive in the strongly alkaline solvent. These intermolecular bonds may be in the nature of van

der Waals forces, which are generally termed "secondary valences" in the polymer field. If this is so, then a micellar solution is not the same as a molecular solution since the micelle is then an aggregate of molecules which are not held together by true covalent bonds. However, the intermolecular forces may be actual covalent bonds which would serve to make the entire micelle one giant molecule. Such bonds are probably not 1,4-β-glucosidic ones, which in cellulose are the primary valence forces. These bonds may be the open-chain acetal type as suggested by Pacsu [16] or any other true covalent bonds such as Haworth's [8] "polymeric bonds" which cross-link the cellulose chains into a three-dimensional micelle. In such a case the cellulose micelle is in fact the fundamental molecule and the distinction between a molecular and a micellar solution disappears. If the molecular structure of cellulose is actually such that the individual molecule is a micelle, then a true statistical distribution of substituents can never arise, since all the hydroxyl groups can never be available for reaction even in a homogeneous solution.

The fact that homogeneous methylation does not proceed exactly according to the laws of probability strongly suggests that the particles in solution are not simple, long chains of anhydroglucose units. It is clearly valid to postulate a micellar dispersion of cellulose in this particular solvent, although it is not possible to suggest how such a micelle is held together. It is important to note that the cellulosic material used for the homogeneous methylation is hydroviscose with a very low degree of polymerization. If this low-molecular-weight material does not appear to form a true molecular dispersion, it cannot be expected that in solution cellulose with a high degree of polymerization would exist in any state other than a micellar dispersion.

The divergence of the experimental distribution curves from the theoretical values can be explained in another way if one wishes to adhere to the assumption that all hydroxyl groups are available for reaction. The theoretical curves were calculated on the assumption that a molecular dispersion exists and also that the reactivity of a particular hydroxyl group is not altered by the methylation of another hydroxyl group in the same glucose unit. If the presence of a methoxyl group in any way enhances the reactivity of either of the other two remaining hydroxyl groups, then the amount of trimethyl glucose will be greater than would be expected from a random distribution of substituents. Such enhancement of reactivity is not likely, although there is no definite experimental evidence available that would rule out this possibility. In summation, then, the divergence of the experimental distribution curves is valid proof for the incorrectness of the assumption either that cellulose is molecularly dispersed or that the reactivity of a hydroxyl group is not altered by the introduction of a methoxyl group into another position in the same glucose unit. Since it is to be expected that the reactivity of a hydroxyl group would be retarded rather than enhanced by a neighboring hydroxyl group substitution, it seems more probable that the assumption of a molecular dispersion is invalid and that cellulose is dispersed as micelles in the particular solvent under investigation.

When the experimental distribution curves for the commercial Methocel are examined in Figures 10 to 13, it is evident that these lie closest to the theoretical distribution curves. At first, this is most surprising since the fact that solid alkali cellulose is the raw material used for methylation makes this product an example of a heterogeneously prepared methyl cellulose. Despite the heterogeneity of the commercial methylation reaction, the substituents distribute themselves even more randomly than in the homogeneous laboratory methylation. As was pointed out, the active methylating reagent is gaseous methyl chloride, which is reacted with alkali cellulose under pressure. The commercial Methocel is therefore the product of a heterogeneous solid-gas reaction and differs in that respect from the laboratory heterogeneous methyl cellulose, which is the product of a solid-liquid reaction. The close adherence of the experimental distribution curves to the theoretical values indicates that virtually all the hydroxyl groups are available for methylation in the solid-gas reaction. Since this appears to be true despite the solid alkali cellulose substrate, it is evident that the hydroxyl groups are available only to the small gaseous methyl chloride and not to the large liquid dimethyl sulfate. The results from the heterogeneous methylation were explained by proposing a topochemical reaction on the alkali cellulose, since the dimethyl sulfate was only able to attack the surface of the fibers. The methyl chloride in the commercial methylation is not restricted to a surface reaction, since this reagent is small enough to diffuse easily into the inner portion of the fibers.

These considerations make it obvious that a statement regarding the availability of the hydroxyl groups is indeed relative. Hydroxyl groups may not

be available for a particular reagent such as dimethyl sulfate, although they may be completely available to another reagent such as methyl chloride.

Conclusions

The following conclusions may be drawn regarding the nature of the cellulose methylation reaction:

1. Heterogeneous methylation using 45% sodium hydroxide solution and dimethyl sulfate is an example of a macroheterogeneous topochemical reaction. This gives rise initially to a product where the fiber surface is preferentially substituted while the inner core of the fiber remains relatively unreacted. Continued methylation proceeds by slow diffusion of the reagents through the methylated fiber surface to the inner unmethylated portion.

2. Homogeneous methylation where cellulose dissolved in trimethylbenzylammonium hydroxide is alkylated with dimethyl sulfate yields products where the substituents are nearly randomly distributed. The significant divergence from the theoretical distribution values indicates that the cellulose is micellarly dispersed and that a true molecular dispersion is not obtained.

3. Commercial methylation where solid alkali cellulose is alkylated under pressure with gaseous methyl chloride gives rise to products which adhere most closely to the theoretical distribution curves. This suggests that virtually all hydroxyl groups are available for reaction with the small gaseous methyl chloride molecules regardless of the heterogeneous nature of the reaction.

4. By determining the distribution of substituents in a given methyl cellulose it is possible to diagnose the method of methylation that was employed.

5. The identification of 2-monomethyl glucose and 3-monomethyl glucose and the absence of 6-monomethyl glucose in all the products regardless of the degree of substitution indicates that the two secondary positions in the glucose unit are more reactive towards alkaline-catalyzed methylation than the primary position. Since the dimethyl glucoses can only arise by the further methylation of the monomethyl glucose units, considerable significance may be ascribed to the absence of 3,6-dimethyl glucose. This isomer can only arise from the methylation of 3-monomethyl glucose since no 6-monomethyl glucose is present. The absence of 3,6-dimethyl glucose therefore indicates that a methoxyl group in the 3 position activates only the 2 position and, if anything, deactivates the 6 position toward methylation. Since both 2,3-dimethyl glucose and 2,6-dimethyl glucose are found to be present, it is probably correct to assume that a methoxyl group in the 2 position equally activates the 3 and 6 positions. It is possible, of course, that only the 6 position in 2-monomethyl glucose becomes reactive, giving rise to the 2,6-dimethyl glucose isomer, while all of the 2,3-dimethyl glucose originates from the 3-monomethyl glucose where the 2 position becomes reactive.

Acknowledgment

This work was carried out as a part of the general research program of Textile Research Institute. One of us (L. R.) is grateful to Textile Research Institute for the fellowship grant which made this work possible.

Literature Cited

1. Blom, J., and Rosted, C. O., *Acta Chem. Scand.* **1**, 32 (1947).
2. Bock, L. H., *Ind. Eng. Chem.* **29**, 985 (1937).
3. Brownsett, T., and Clibbens, D. A., *J. Textile Inst.* **32**, T32 (1941).
4. Clark, E. P., *J. Assoc. Offic. Agr. Chemists* **15**, 136 (1932).
5. Compton, J., *J. Am. Chem. Soc.* **60**, 2832 (1938).
6. Denham, W. S., and Woodhouse, H., *J. Chem. Soc.* **103**, 1735 (1913).
7. Dimler, R. J., Schaefer, W. C., Wise, C. S., and Rist, C. E., *Anal. Chem.* **24**, 1411 (1952).
8. Haworth, W. N., *Chemistry & Industry* **58**, 917 (1939).
9. Hirst, E. L., Hough, L., and Jones, J. K. N., *J. Chem. Soc.* **1949**, p. 928.
10. Johnston, G. G., *J. Am. Chem. Soc.* **63**, 1043 (1941).
11. Lemieux, R. U., and Bauer, H. F., *Can. J. Chem.* **31**, 814 (1953).
12. Lippoid, U., *Biochem. Z.* **323**, 115 (1952).
13. Mahoney, J. F., and Purves, C. B., *J. Am. Chem. Soc.* **64**, 9, 15 (1942).
14. Mehta, P. C., and Pacsu, E., TEXTILE RESEARCH JOURNAL **18**, 387 (1948).
15. Monier-Williams, G. W., *J. Chem. Soc.* **119**, 803 (1921).
16. Pacsu, E., TEXTILE RESEARCH JOURNAL **17**, 405 (1947).
17. Partridge, S. M., *Nature* **158**, 270 (1946).
18. Partridge, S. M., *Nature* **164**, 443 (1949).
19. Spurlin, H. M., *J. Am. Chem. Soc.* **61**, 2222 (1939).
20. Steele, R. O., and Pacsu, E., TEXTILE RESEARCH JOURNAL **19**, 771 (1949).
21. Timell, T., "Studies on Cellulose Reactions," Stockholm, Sweden, Esselte Aktiebolag, 1950.
22. Traube, W., and Funk, A., *Ber.* **69**, 1476 (1936).
23. Vieböck, F., and Schwappach, A., *Ber.* **63B**, 2818 (1930).
24. Wolfrom, M. L., and Binkley, W. W., "Chromatography of Sugars and Related Substances," *Scientific Report Series* No. 10, Sugar Research Foundation, Inc., New York, Aug. 1948.

(*Manuscript received August 25, 1954.*)

A Microscopical Study of the Effects of Some Typical Chemical Environments on the Primary Wall of the Cotton Fiber

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Abstract

The topography and structure of the primary wall of the cotton lint fiber are described and illustrated by electron micrographs. The changes in this thin membrane brought about by alkali boil (kiering), hypochlorite and peroxide bleaching, mercerization, acid hydrolysis, and dry heat are shown by means of microscopical examination of isolated pieces of the primary wall after exposure to these environments. The noncellulosic constituents of the wall, which account for a large part of its chemical composition, are progressively removed during alkaline kiering. Excessive conditions of kiering appear to damage the cellulose framework of the wall. Peroxide bleaching is apparently effective in removing the encrusting noncellulosic material, but hypochlorite alone does not have this effect. Mercerization of the isolated wall induces shrinkage in both longitudinal and transverse directions; the shrinkage increases when the noncellulosic materials are removed from the membrane prior to mercerization. The morphology and structure of the wall account for the observed behavior on mercerization, and electron micrographs of the mercerized wall show a shrunken network of cellulose fibrils. The primary wall shows resistance to disintegration by acid hydrolysis, and its fibrillar pattern is preserved intact, after long periods of contact with hot mineral acid. Long periods of heating in air "set" the primary wall in a configuration similar to that which it had on the corrugated surface of the cotton fiber.

The contribution of the primary wall to certain gross properties of the fiber and its behavior during finishing treatments is discussed.

SUCCESSFUL interpretations of phenomena occurring during the commercial finishing treatments and usage of cotton textiles have been accomplished by observations of changes wrought by these environments on the gross properties and fine structure of the fibers. However, morphological changes which the structural components of the fiber undergo are difficult to observe visually in many cases, although such examinations generally contribute to sounder explanations of the phenomena involved. For this reason, attempts to bridge the gap between the gross and fine structure of cotton have led to extensive microscopical study of the fiber for the past half century.

More recently, the application of electron microscopy, the high resolution of which permits visualization of the "ultrastructure" of cellulosic materials, has yielded information which makes possible extension of earlier concepts. As with light microscopy, lack of contrast or interference of other fiber components hinders full exploitation of this type of observation; its general use is as yet severely limited by the special conditions necessary to observe specimens and the difficulties of specimen preparation. All forms of microscopy, nevertheless, must be regarded as important tools in the attack and solution of structural questions, for in the field of textiles, as well as in that of any technology, there is a continuing demand for qualitative or quantitative correlation between the structure of a material and its performance in use.

As the present status of specimen preparation for electron microscopy is largely developmental, straightforward or simple methods are seldom available for use in any given field of study. The reduction of fibers or fiber components to suitable thicknesses for electron microscopy often may involve destruction or distortion of the original structure or arrangement, with attendant creation of artifacts. One approach to the examination of fiber structure,

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originally developed for the study of metals, is the replication of the surface of the object in stable films thin enough for transmission of the electron beam. The study of the structure of the entire fiber by this method must necessarily be stepwise, but such imprinted replicas are capable of yielding information of reliability and precision. The obvious approach by means of thin sections of the fiber has not shown much promise as yet; the technique for production of ultrathin sections (*ca.* 0.1 μ) of many types of organic material, including cotton, is by no means a routine accomplishment at this stage of development.

The generally recognized lamellate arrangement of the cotton fiber cell wall makes the outer surface a logical point of attack in structure studies, because more detailed information can be obtained on it than on the inner regions of the cell wall. The accessibility of the primary wall to examination is apparent from consideration of the fact that during most of the period of its extension during growth it is entirely free from the bulk of the fiber which develops later. The feasibility of removal and isolation of this membrane in a relatively intact state from fully grown fibers likewise permits microscopic observation without interference from other fiber components. Kling and Mahl [8–10] in a recent study of cotton fiber structure examined the morphology of this thin outer membrane with both light and electron microscopes. They employed the replica technique for their electron microscopical studies with good success.

However, in the work reported here, most of the observations were made on portions of the primary membrane isolated from cotton fibers. Replicas of the surface of fibers were also studied, but the inherently greater resolution possible in the use of the membrane itself makes interpretation of micrographs easier and more reliable. Specimens of the primary wall isolated by beating were examined after subjecting them to a variety of chemical treatments simulating commercial processing conditions, including kiering, bleaching, and mercerization; changes induced by exposure to heat in air and to acid hydrolytic conditions were also studied.

In consideration of the technological aspects of cotton fiber morphology, the unique role of the primary wall has been generally recognized. Although probably amounting to less than 5% of any normal fiber, the location, chemical composition, and structure of this membrane make it an important factor in fiber behavior. As the outer covering of the fiber, it comes into immediate contact with physical environments; as the site of high concentrations of the noncellulosic constituents of the fiber, it is an important target in commercial purification operations; and its morphology enhances its function as the limiting and constricting member in fiber swelling. Its structure is likewise of interest in throwing light on the complicated mechanism of growth in the higher plants. The description of the structure and behavior of the wall reported herein may be regarded as an extension of earlier concepts on these points. As in the case of the work of Kling and Mahl [8–10], the results of such studies may lead to revision of views hitherto generally held concerning fiber structure.

Nature and Structure of the Primary Wall

Physical Nature

In the fully grown cotton fiber of commerce, the primary wall encases the predominantly cellulosic body of the fiber and is closely molded to it, although small discontinuities may be present as a result of mechanical damage or abrasion. The removal of any large fraction of this outer sheath from the fiber is ordinarily difficult, but in the case of untreated fibers portions of the primary wall may be loosened and freed from the fiber by beating the fibers in water in a Waring Blendor * [14, 21]. After any of a variety of treatments, however, such as kiering, mercerizing, heating, etc., the primary wall cannot be freed from the fiber to an appreciable extent by wet beating. Since each of these treatments alters the physical and chemical state of the wall, such behavior might be expected, particularly in the light of the structure of the primary wall as described below.

The contiguity of the primary wall and of the layers of the cell wall beneath it is shown in Figure 1. In this electron micrograph a fiber from a boll picked 17 days after flowering has been mechanically damaged and the primary wall is seen torn back to expose the tiny fibrils of secondary thickening beneath it. The surface of the outer membrane is comparatively featureless and smooth even at this high magnification. It must be recalled that such observations are carried out in high vacuum, resulting in desiccation of the specimen; the resolution ap-

* Mention of trade names does not constitute endorsement by the Department of Agriculture over similar products not mentioned.

parent in the electron microscope image, as a result of adequate penetration of the specimen by the electron beam, indicates that the total thickness of the dry fiber specimen is less than 0.3 μ. In contrast to the unruffled surface of the young fiber is the surface of a fully grown fiber, reproduced by the replica technique, and shown in Figure 2. By this method [5], an impression of the fiber surface is taken in softened polystyrene film, a thin deposit of silicon monoxide or dioxide is evaporated *in vacuo* vertically on the polystyrene impression, and the polystyrene removed by cautious solution with carbon tetrachloride. The silicon oxide "positive" replica thus produced is metal-shadowed [5] to emphasize surface irregularities. In the older fiber, numerous grooves and ridges are present, running at an angle roughly corresponding to the direction of the secondary wall fibrils seen in Figure 1. The closeness of the primary wall to the underlying fiber body is evident.

When separated from the untreated fiber by wet beating, the primary wall flattens out in the form of sleeves or sheets. As is evident from Figures 1 and 2, as well as from observations with the light microscope, the membrane is exceedingly thin, being less than 0.1 μ thick in the dry state. A body of such dimensions would be expected to possess small mechanical strength, and rupture and tearing of the membrane frequently do occur during manipulation. Therefore, it is improbable that the primary wall makes a significant contribution to the tensile strength of normally developed fibers.

The isolated primary wall exhibits no apparent structure when viewed with ordinary transmitted light. Between crossed nicols, a system of bands transverse to the fiber axis appears, particularly when the wall is stained with a substantive dichroic dye [1]. The appearance of the wall in the electron microscope is shown in Figure 3, where a sleeve (double thickness) of untreated wall isolated from a mature fiber has been mounted upon a supporting formvar film. While no characteristic structural pattern is evident, the presence of tiny fibrils is ap-

FIG. 1. *Electron micrograph of 17-day-old cotton fiber, with primary wall torn to expose secondary thickening beneath. Palladium shadowing.*

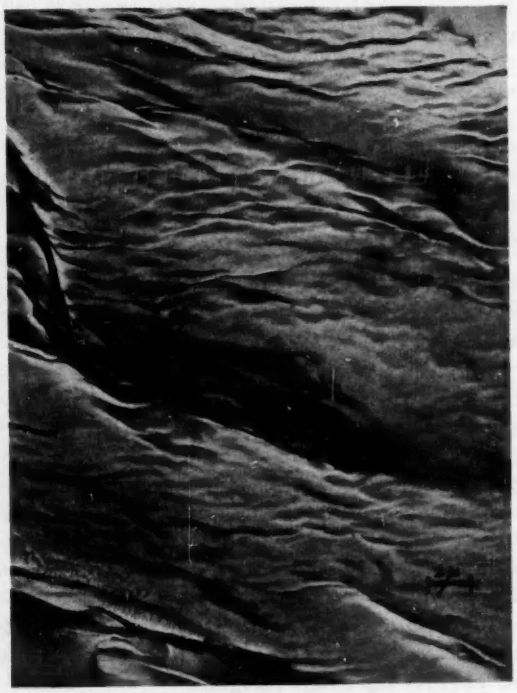


FIG. 2. *Electron micrograph of replica of surface of fully grown cotton fiber. Polystyrene-silicon monoxide method. Palladium shadowing. Positive print.*

parent upon close inspection, particularly in the original micrographs. A coating of amorphous material conceals the fibrils at most points in the specimen. The small sphere seen in Figure 3 is a polystyrene latex particle about 0.26 μ in diameter [5]. By comparison with such objects, the extreme thinness of the primary wall may be visualized readily.

Chemical Nature

Chemical analyses of the primary wall isolated from commercial fibers have been reported [21, 22]. Approximately 50% of the wall is cellulose; the major part of the remainder consists of wax (alcohol-solubles, 8%), pectic substances (10%), and nitrogenous material (13%, expressed as protein). Thus, in terms of the chemical composition of the whole fiber, the noncellulosic substances are highly concentrated in the primary wall. For this reason, the application of certain biological stains results in a much more intense coloring of the primary wall than of the interior cell wall of the fiber [13].

An attempt was made to estimate the degree of polymerization of the cellulose of the primary wall by viscosity measurements. Since sufficient material could not be isolated from fully grown fibers, the fibers from 11- to 13-day-old bolls were dispersed in cuprammonium hydroxide. These dispersions were filtered and centrifuged before their viscosity was measured. The cellulose content of the developmental material was determined independently by extraction with monoethanolamine, followed by measurement of weight loss in cuprammonium hydroxide. The ethanolamine-extracted material appeared to have a large amount of seed fragments present, which accounted for the low (20%) cellulose content of the starting material. The method of Tripp, Conrad, and Mares [20] was employed to estimate the intrinsic viscosity; the results indicated a degree of polymerization in the range 3,000 to 5,000. This is in the range usually associated with undegraded cotton cellulose.

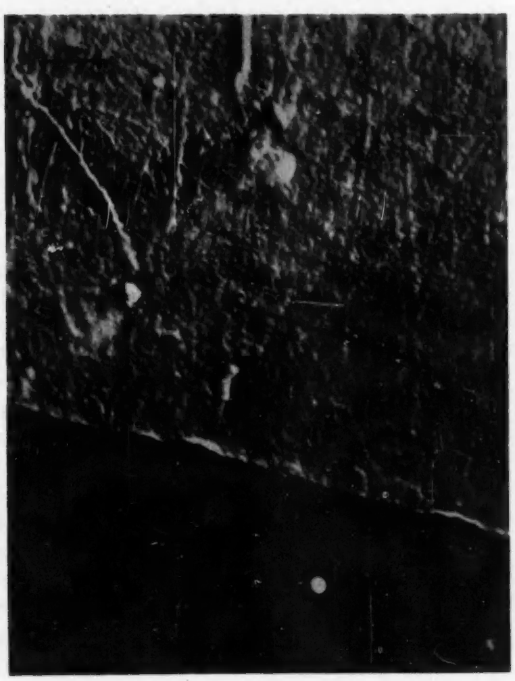


FIG. 3. *Electron micrograph of sleeve of untreated primary wall of cotton fiber. Arrow indicates axial direction of fiber. Palladium shadowing. Sphere is polystyrene latex particle used as reference object for calibration.*

FIG. 4. *Electron micrograph of sleeve of primary wall of cotton fiber, extracted with ethyl alcohol and with monoethanolamine. Arrow indicates fiber axis. Chromium shadowing.*

Arrangement of Cellulose and Noncellulosic Materials

The spatial relationships of the cellulosic and noncellulosic portions of the primary wall may be revealed, within limits, by electron microscopy of the wall after extraction of the various noncellulosic materials present. If waxy substances are removed by solution in ethyl alcohol, and pectic and nitrogenous material by digestion with monoethanolamine, a woven network of minute cellulosic fibrils appears. This cellulosic structure has been described by a number of workers, including O'Kelley [15], Roelofsen [17], Kling and Mahl [10], and Mühlethaler [14], who found that this pattern was characteristic of the primary walls of a number of plant fibers. Whether primary walls from young or fully developed fibers are examined, the cellulose framework appears to be similar. Figure 4 is an electron micrograph of a sleeve of primary wall from a mature fiber, after extraction with ethyl alcohol at 60°C for 1 hr. and with monoethanolamine at 160°C for 4 hrs. It is obvious that the noncellulosic material removed by the extraction procedures was located on the outer surface of the membrane and between the cellulose fibrils. After extraction with ethyl alcohol only, the cellulose fibrils are more distinct than in the untreated wall, but the removal of wax in this manner does not indicate that it alone forms the surface of the wall. Attempts to remove the cellulose from the noncellulosic matrix that surrounds it by cautious treatment with cuprammonium hydroxide solution did not yield patterns that could be recognized in the electron microscope; undoubtedly some of the cellulose was removed, but the accompanying swelling appeared to disturb the remaining material to a great extent. It may be concluded that the "amorphous" noncellulosic substances occupy nearly all available space between the fibrils.

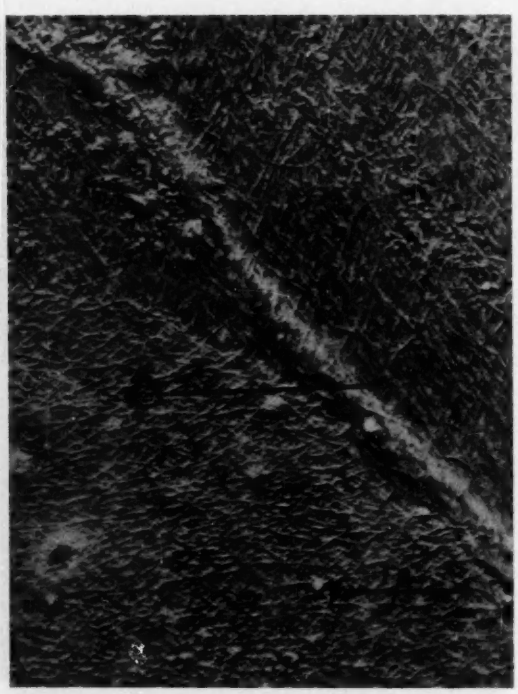


FIG. 5. *Electron micrograph of torn end of sleeve of purified primary wall, showing both inner and outer surfaces of cellulose phase. Arrow indicates axial direction of fiber. Chromium shadowing.*

While some specimens of purified primary wall show no particular orientation of the cellulosic fibrils present, the existence of oriented systems may often be demonstrated [17]. Figure 5 shows the torn end of a sleeve of purified primary wall arranged in such a fashion as to display both outer and inner surfaces of the cellulosic framework. On the outer surface, shown at the lower left of this figure, a system of fibrils is predominantly oriented in a direction roughly parallel to the fiber axis. The inner surface, in the right portion of the micrograph, shows interwoven fibrils lying in a more transverse direction. The geometric regularity of the transverse system in this specimen is particularly striking. Indications of this pattern of arrangement may be found in other micrographs of this paper. Frey-Wyssling's idealization [3] of the cellulose pattern of primary walls approximates that of a woven fabric; the longitudinal fibrils may be regarded as the warp and the transverse fibrils as the filling. Inspection of micrographs like Figure 5 reveals that the transverse system is predominant in the wall. The transverse striations seen in primary walls in the polarizing microscope are thus due to the higher concentration of fibrils oriented in this direction; the axially oriented fibrils are too widely scattered to show birefringence under the conditions of examination. The negative birefringence of the primary wall, as shown by its polarization colors, is additional evidence of this.

The diameter of the cellulose fibrils of the primary wall varies from 100 to 400 angstrom units. Their length appears to be several microns and may

be greater. It is possible that the wider fibrils consist of two or more of the narrower, for in extensively purified specimens the fibril diameters appear to have greater uniformity.

Effects of Typical Treatments

Alkaline Kiering

One of the principal aims of the commercial kiering process is to achieve partial or complete removal of "foreign" substances from cotton to provide a more uniform cellulose substrate for subsequent finishing operations or use. The high proportion of noncellulosic material in the primary wall of the fiber puts this membrane in a strategic position to interfere with treatments designed to affect the entire fiber. The increase in cellulose percentage, whiteness, and absorbency of cotton following kiering, along with changes in the swelling patterns and staining responses of the fibers, has led to the general impression that the primary wall is destroyed by kiering, and that the behavior of kiered fibers is characteristic of secondary wall cellulose exclusively. Electron microscopical studies of the effects of kiering on the primary wall do not bear out these generalizations, but indicate that the primary wall, and in particular its cellulose framework, maintains its integrity for long periods of time under the conditions of kiering.

The mechanism of removal of noncellulosic material in cotton by alkali is not completely understood, but certain aspects of the process appear to be established. Pectic substances are solubilized by conversion to their alkali derivatives (salts), probably with accompanying depolymerization; replacement of polyvalent cations by sodium, for example, appears to be an essential part of the reaction [24]. The removal of pectic matter has been shown to be relatively rapid under treatment with hot alkaline solutions, as is also the case with nitrogen-containing substances in cotton. Wax, however, is removed more slowly, and, indeed, incompletely by most kiering procedures [12]. The time required for solubilization of wax by saponification or emulsification may hinder temporarily exposure of the more hydrophilic alkali-labile substances of the fiber, particularly in the primary wall where these substances appear to be intimately associated with the wax.

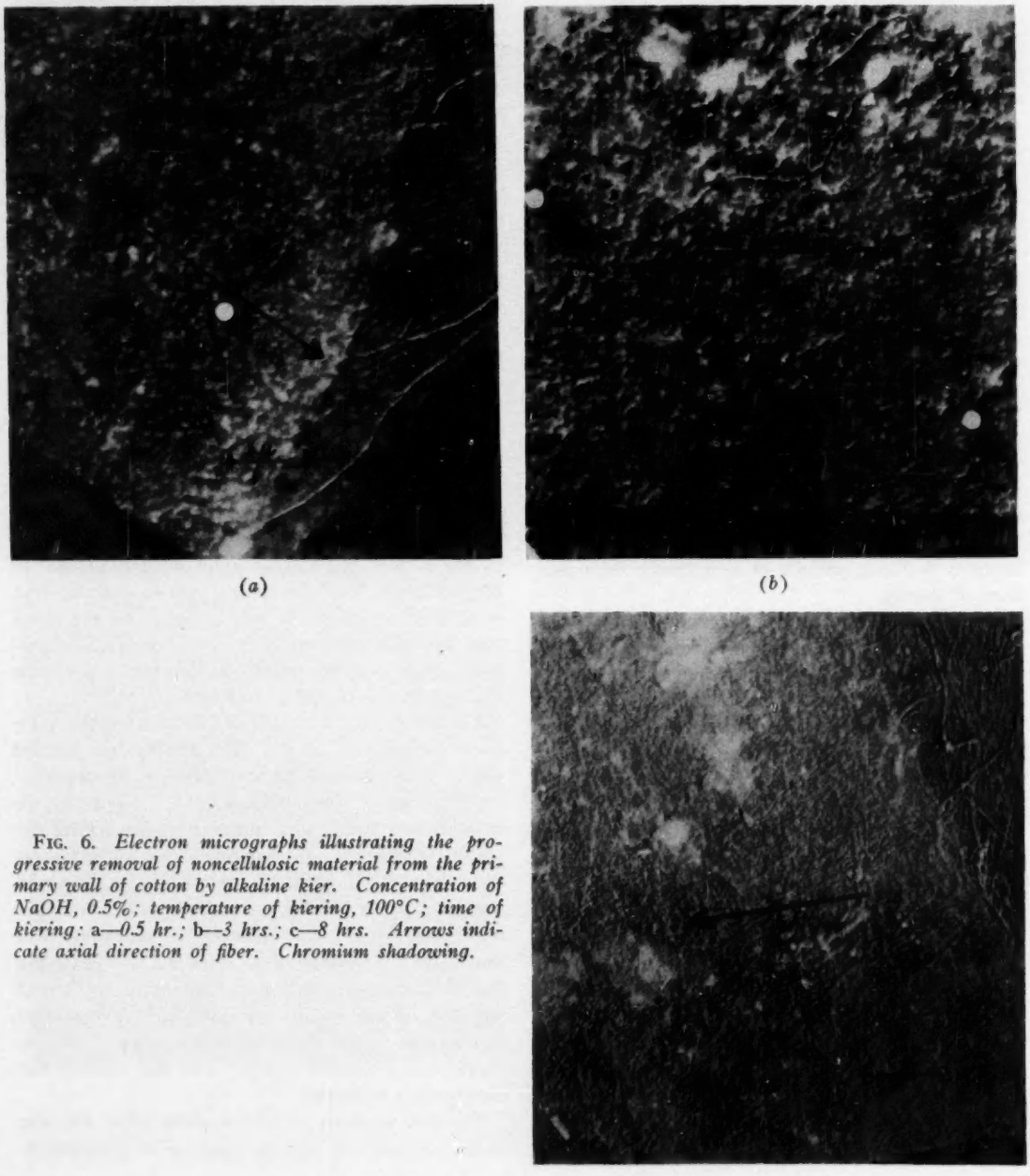
A wide variety of conditions are presently employed in commercial kiering, but caustic soda has become the reagent of choice because of its economy and effectiveness [12]. Typical kier solutions contain 1% to 2% NaOH, with or without auxiliary reagents, and are employed in such quantity as to give a 1 to 3:100 alkali-goods ratio [12, 4]. Temperatures of kiering range from 100°C (open kier) to 145°C (45 p.s.i.), and periods of kiering may range from a few hours to a day. Since the conditions used affect the end result to some extent, wide variations in concentration, time, and temperature are practiced in achieving the desired product.

In attempting to simulate some aspects of large-scale kiering on microscopic amounts of isolated primary wall material, some consideration was given to the concentration of alkali in the solutions used. In commercial kiering, the initial concentration of alkali may be rapidly lowered. Viktoroff and Goldberg [23] measured the free alkali content of the kier liquor at various stages of a full-scale process (alkali-goods ratio 3:100), and found that a liquor originally containing 13.2 g./l. of NaOH dropped to 5 g./l. after 1 hr. of kiering and to 3 g./l. after 4 hrs. A second kiering of the goods with fresh alkali showed a decrease in NaOH concentration from the initial 13.2 g./l. to 6 g./l. after 1 hr., with little further decrease thereafter. They attribute the decreases to salt-formation and absorption of the alkali by the cotton; dilution by water initially present in the wet goods may also have occurred. In the light of these observations, it was thought that the alkali concentration with extremely small amounts of primary wall present would be essentially constant throughout the period of treatment.

Concentrations of NaOH of 0.5% and higher were used, as indicated below. The kiering was carried out in small beakers or test tubes, using approximately 10 ml. of the alkaline solution. Generally, no discoloration of the kier liquor occurred during the periods employed. In experiments at kiering pressures above atmospheric, an ordinary household pressure cooker to which a pressure gage had been fitted was used. The sequence of operations followed was essentially that described by Kettering and Kraemer [7], including washing of the kiered material with dilute acid and distilled water prior to examination. No desizing was required, as the fibers from which the primary wall was isolated had no previous treatment.

The low intensity of stains which color the wax of the primary wall makes their use in demonstrat-

ing the amount of wax in the wall impracticable, but staining with ruthenium red or Nile blue sulfate gives a rough index of the amount of pectic material present. The limitation of the stain to the primary wall of the fibers may be confirmed by swelling in cuprammonium hydroxide, which ruptures the outer wall to expose the fiber body beneath. Although the affinity of such basic stains for acidic groups in oxycellulose tends to vitiate their reliability for detection of pectic substances and calls for caution in the



(*a*) (*b*) (*c*)

FIG. 6. *Electron micrographs illustrating the progressive removal of noncellulosic material from the primary wall of cotton by alkaline kier. Concentration of NaOH, 0.5%; temperature of kiering, 100°C; time of kiering:* a—*0.5 hr.;* b—*3 hrs.;* c—*8 hrs. Arrows indicate axial direction of fiber. Chromium shadowing.*

interpretation of microscopical observations, the intensity of staining of the primary wall may be seen to be greatly reduced as noncellulosic substances are removed from it.

A laboratory procedure for the determination of cellulose in cotton involves extraction of the wax with hot ethyl alcohol, followed by digestion of the fiber with monoethanolamine at elevated temperatures (*ca.* 170°C for 2 or more hours [19]). Such procedures yield purified cottons approaching 100% in cellulose content. This method of purification was adopted as a criterion of the effectiveness having the same general aim—removal of noncellulosic material from the primary wall of other treatments. The appearance in the electron microscope of the cellulosic framework of the wall, as judged by its freedom from impregnating material after such purification, was used as a basis for comparison.

That kiering removes material coating and impregnating the cellulose fibril framework progressively with time is illustrated by the series of micrographs in Figure 6. The sleeves of primary wall shown were kiered with 0.5% NaOH at 100°C for 0.5, 3, and 8 hrs., respectively. Although the surface of the wall appears to be disturbed after the shortest time of kiering (Figure 6a), as compared with untreated material (Figure 3), the underlying fibrils are not clearly seen until after the 3-hour interval (Figure 6b); and the effective removal of the encrusting substances is accomplished only after a longer period, yielding the well-defined cellulose fibrils seen after 8 hrs. of kiering (Figure 6c).

An attempt was made to observe the effect of wetting agents in the kier on the rate of removal of noncellulosic material. In separate experiments, an alkali-resistant anionic wetting agent was added to the kier solution to produce a concentration of 0.2%. The appearance of the primary wall from these kierings was not different from that of the specimens kiered without wetting agents present. It is possible that the effectiveness of soaps and other detergents in commercial kiering operations lies in their capacity to produce rapid and thorough wetting-out of yarn and fabric structures. Brief periods of boiling in aqueous solutions of detergents alone brought about no change in the appearance of the primary wall.

The use of high concentrations of alkali and higher temperatures of kier for longer periods of time was attended by some apparent damage to the arrangement of the wall. Figure 7 shows a sleeve of primary wall kiered with 3.5% NaOH at 120°C for approximately 8 hrs. Loose ends of cellulose fibrils are apparent, and few longitudinally oriented fibrils are visible on the surface. A specimen kiered for 6 hrs. with 2% NaOH at 120°C is shown in Figure 8. Here the longitudinal system of fibrils has been preserved, but the removal of encrustants is not as complete as in the specimens in Figure 7 or Figure 6c.

In some finishing plants, a double kier boil may be employed. A kier boil with 2.5% NaOH for 3 hrs., followed by souring, washing, and a kier boil with 1% NaOH for 6 hrs. has been cited [7]; both operations were carried out at 120°C. The application of this treatment to the primary wall showed that it was effective in removing the noncellulosic matter without damage to the cellulose framework. A specimen which underwent this sequence of operations is shown in Figure 9. The cellulose structure showing longitudinal fibrils overlying those more transverse to the fiber axis is evident.

FIG. 7. *Electron micrograph of sleeve of primary wall kiered for 8 hrs. at 120°C with 3.5% NaOH. Chromium shadowing.*

The freedom of the cellulose framework of the isolated primary wall from encrusting material after periods of kiering corresponding to commercial procedures compares favorably with that produced by the laboratory alcohol-monoethanolamine process. Large-scale kierings appear to leave about one-third of the original wax present in the fiber [7, 12]. If the laboratory purification of the primary wall by the methods reported herein removes all of the wax present, it may be thought that large-scale operations on the fiber are less effective because of the inherent difficulty in completely solubilizing the wax and washing it out of the fabric. It must be recalled, however, that very efficient wax removal gives fabrics an undesirably harsh hand [12].

As pointed out by Kling and Mahl [9], whose studies on kiering involved conditions even more severe than those used in this work, the integrity of the cellulose structure of the primary wall can be damaged by alkaline cooking. While the literature contains references to the destruction of the primary wall by alkali boil, the experiments outlined here, as well as those of Kling and Mahl, indicate that this can be accomplished only under extreme and prolonged conditions. In the sense that the noncellulosic "cuticle" of the fiber is removed by such treatment, thus profoundly affecting the functionality of the membrane and of the fiber surface, it may be said that the primary wall is "destroyed" by ordinary kiering.

A simultaneous examination of both inner and outer surfaces of the primary wall, that occasionally occurs by fortuitous placement of the specimen, permits certain conclusions to be drawn about the relative thickness of the noncellulosic phase on these surfaces. In Figure 3, a small tear in the upper side of the primary wall sleeve reveals the inner surface of the wall. In the untreated state the fibrils are more distinct on the inner surface than on the outer. In Figure 6 primary wall sleeves have torn ends which allow the outer and inner surfaces of the wall to be seen. At the early stage of removal of encrust-

FIG. 8. *Electron micrograph of sleeve of primary wall after kiering with 2% NaOH at 120°C for 6 hrs. Chromium shadowing.*

FIG. 9. *Electron micrograph of sleeve of primary wall after double kier boil (2.5% NaOH for 3 hrs., followed by 1% NaOH for 6 hrs.; both operations at 120°C). Chromium shadowing.*

ing material (Figure 6a), the outer surface is still coated with noncellulosic matter. It thus appears that the noncellulosic material of the primary wall exists in a thicker film on the outer surface than on the inner. The effects of mercerization on the primary wall, discussed below, lend credence to this conclusion.

Oxidative Bleaching

While the noncellulosic materials present in the primary wall of cotton may not contribute appreciably to the slight off-white color of the unbleached fiber, it has been shown that oxidative bleaching reduces the amount of some of the noncellulosic substances present [7]. In the present study, the effect on the appearance of the primary wall of exposure to sodium hypochlorite and to hydrogen peroxide, the two most widely used bleaching agents, was examined. As in the case of kiering, the bleached wall was compared with specimens purified by the alcohol-monoethanolamine laboratory method. The hypochlorite used was a commercial household bleach solution diluted to give a density of 1.004 g./cc. ($\frac{3}{4}$° Tw.); analysis showed this dilution to contain 0.7 g. available Cl/1. The pH of the diluted hypochlorite was 9.0. Three percent (10 volume) hydrogen peroxide was diluted to 0.15% (0.5 volume) strength and made alkaline to pH 10 to 11 with sodium silicate or ammonium hydroxide. Isolated sleeves of primary wall were exposed to these solutions before and after kiering. The hypochlorite was used at room temperature, and the peroxide at 83°C. The specimens were thoroughly washed with water prior to microscopical examination.

Soaking of untreated primary wall in the hypochlorite for 1 hr. or more had no effect on the appearance of the wall in the electron microscope. After such treatment, the wall stained vividly with ruthenium red or Nile blue, indicating the continued presence of pectic material. Bleaching with hypochlorite after kiering appeared to render the cellulose fibrils of the wall somewhat more free of nonfibrillar material than did kiering alone, but it was evident that the major portion of the noncellulosic substances had been removed in the kiering process.

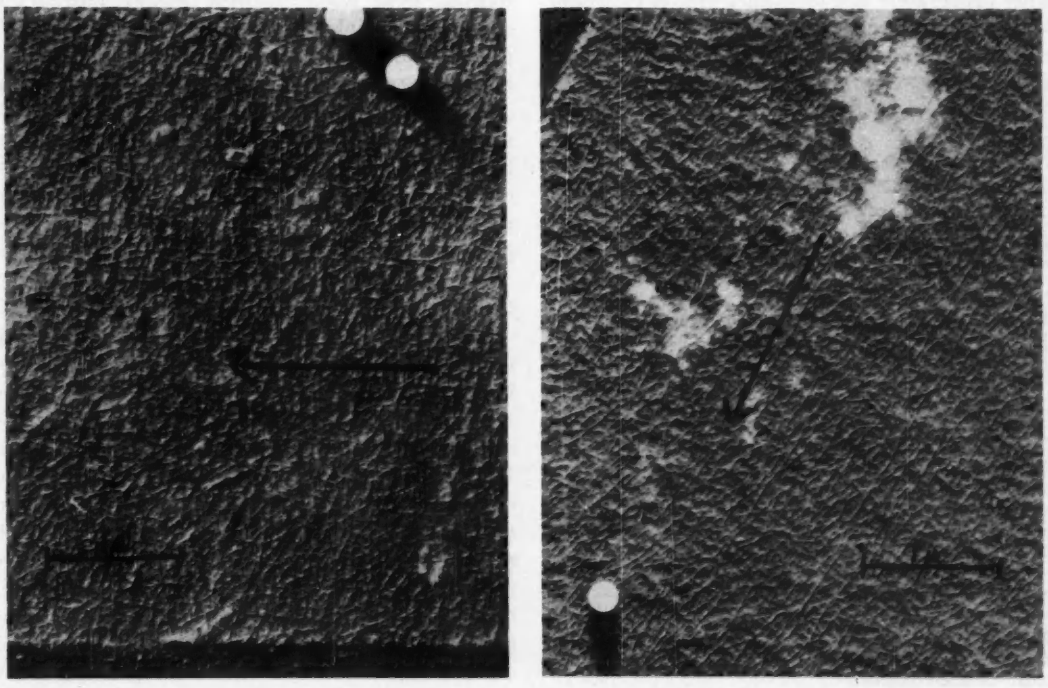


FIG. 10. *Electron micrographs of sleeves of primary wall bleached with 0.15% hydrogen peroxide at 83°C for 3.5 hrs.* Left,—*silicate-buffered;* right,—*ammonia-buffered. Palladium shadowing.*

In contrast to the hypochlorite, treatment of unkiered primary wall with hot alkaline peroxide for 3 to 4 hrs. removed the major portion of nonfibrillar material from the cellulose framework. Peroxide buffered with ammonia appeared to be slightly more effective than that buffered with sodium silicate, possibly due to the greater ease of removal of the ammonia solution. Figure 10 shows two sleeves of primary wall treated with 0.15% hydrogen peroxide at 83°C for 3.5 hrs.; the sleeve at the left was bleached with silicate-buffered peroxide, that at the right, with ammonia-buffered peroxide. The axial orientation of the outer fibril system is apparent.

The application of the peroxide bleach to kiered primary wall appeared to produce further removal of material from between the cellulose fibrils. This observation is in line with the finding of Kettering and Kraemer [7], who showed that a greater decrease in noncellulosic substances occurred after peroxide bleaching than after hypochlorite bleaching of previously kiered broadcloth. This difference may be accounted for by the appreciably greater alkalinity of the peroxide bleach, in addition to the higher temperature and the longer time of treatment. No damage to the cellulosic fibril system of the wall was visually apparent after either method of bleaching.

Mercerization

When normal cotton fibers are exposed without restraint or tension to the action of 18% NaOH, they shrink 10% to 15% in length, increase some 20% or more in diameter, and their cross-sectional shape becomes more circular. The shortening of the fiber in the direction in which the majority of the cellulose chains lie—i.e., axially—is responsible, in part, for the increased diameter. The action of the primary wall in limiting this increase has been demonstrated; fibers whose surface had been abraded with emery paper showed greater transverse swelling and longitudinal shrinkage than did unabraded fibers [11]. The restrictive behavior of the outer wall is also reflected in the tendency of the fibers to become more nearly cylindrical, with decreased perimeter, after mercerization and drying [16].

Examination of the architecture of the primary wall with the electron microscope permits a more nearly complete explanation of its role during mercerization of the fiber. An earlier discussion of this phenomenon by Berkley, based largely on chemical and x-ray diffraction data [2], is confirmed in its major points by the present investigation.

In young fibers having no secondary thickening present, or in isolated sleeves of primary wall, shrinkage in both axial and transverse directions occurs on transfer from water to 18% NaOH [18]. The amount of shrinkage was measured on sleeves of primary wall about 1 mm. long, and the data obtained are summarized in Table I. Using a microscope with eyepiece micrometer, the sleeves were measured in water and again after replacement of the water with 18% NaOH. The dimensional changes caused by such mercerization were measured on specimens in the untreated state and after progressive removal of wax and other extractables. The major part of the shrinkage, if not all, appeared to occur instantaneously on exposure to the alkali.

TABLE I. DIMENSIONAL CHANGES OF SHORT LENGTHS OF PRIMARY WALL AND WHOLE FIBER ON TRANSFER FROM WATER TO 18% NaOH

Condition	% Change* Length	Width
Primary wall		
No treatment	− 3 ± 1	−32 ± 2
Wax-free (alcohol-extracted)	−11 ± 1	−38 ± 2
Wax-, pectin-free (alcohol-, ethanolamine-extracted)	−41 ± 2	−57 ± 2
Fiber		
No treatment	−13 ± 1	+20 ± 4
Primary wall removed mechanically	−20 ± 3	+65 ± 9
Wax-, pectin-free (alcohol-, ethanolamine-extracted)	−13 ± 1	+43 ± 4
Commercially purified	−10 ± 1	+28 ± 5

* Average of measurement on 10 specimens of each sample. Figure following ± sign is standard error.

The shrinkage observed seems to be dependent on the extent to which the noncellulosic substances of the wall have been removed. The submicroscopic structure of the primary wall described above lends itself to an explanation for the dimensional changes. In the case of the untreated wall, the axially oriented cellulose fibrils on the outer surface are largely protected by a relatively thick film of materials which restrict the swelling action of the alkali, while the inner transverse system is less effectively covered; thus, the cellulose whose orientation would contribute to lengthwise shrinkage is either not affected or unable to shrink by virtue of its position in the noncellulosic matrix. The small axial shrinkage (3%) of the wall contrasts with the large shrinkage (32%) transversely. After removal of the wax, an

increase in the shrinkage by alkali occurs in both dimensions, indicating a freeing of both fibril systems; the change is more apparent in the axial shrinkage. More complete removal of the noncellulosic materials of the wall produces large increases in both axial and transverse shrinkage. It may be assumed that the shrinkage by alkali in the purified state is characteristic of the cellulose pattern present, as the wall is free of material which would either hinder access of the alkali or inhibit shrinkage.

Unlike the corresponding behavior of whole fibers, the free shrinkage of the wall observed under the microscope is apparently not reversible. When the NaOH was removed, by washing with dilute acetic acid and water, there was no tendency for the wall to return to larger dimensions. When the purified wall thus mercerized and washed is examined in the electron microscope, it is seen that the fibrils have drawn together and are more difficult to distinguish as separate entities. Figure 11 shows a sleeve of purified (by alcohol, monoethanolamine digestion) primary wall after mercerization and washing. The shrunken appearance of the fibrillar network bears out the dimensional change observed with the light microscope.

Also summarized in Table I are measurements on the dimensional changes of short lengths of whole fibers on transfer from water to 18% NaOH. The influence of the removal of the noncellulosic materials from the fiber on the transverse swelling is evident. The even higher swelling of fibers having no primary wall indicates that the cellulose framework of the membrane exercises a restrictive action. The commercially purified fibers exhibited less swelling than those purified in the laboratory possibly reflecting the relative effectiveness of removal of material from the primary wall.

Exposure of the primary wall to mercerizing caustic does not appear to remove any of the encrusting materials from it, as judged by its appearance in the electron microscope as well as by its staining reactions. The swelling of the fiber body, together with the tendency of the primary wall to shrink, generally results in a smoothing of the fiber surface. Figure 12 shows the surface of a mercerized fiber, reproduced by the replica method; the grooves and ridges of the untreated fiber (*cf.* Figure 2) have been eliminated to a marked extent.

The closer bonding of the primary wall to the underlying secondary thickening after kiering or

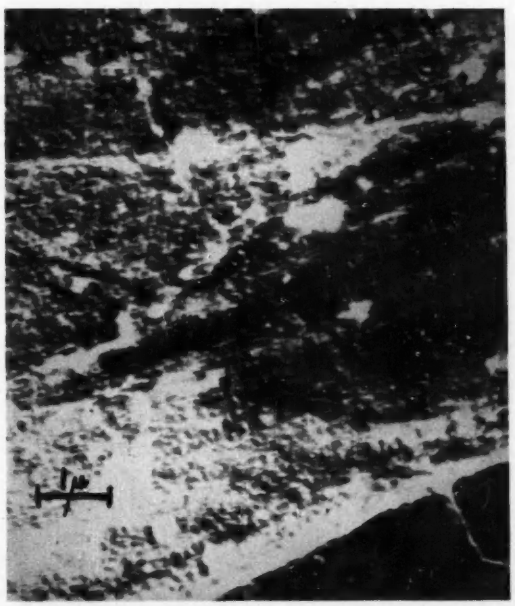


FIG. 11. *Electron micrograph of sleeve of primary wall after purification and mercerization. Arrow indicates axial direction of fiber. Chromium shadowing.*

FIG. 12. *Electron micrograph of surface replica of mercerized cotton fiber. Polystyrene-silicon monoxide method. Palladium shadowing. Positive print.*

mercerization is evidenced by the extreme difficulty of separation by mechanical beating. In both treatments, the material separating the cellulose of the secondary wall from that of the primary wall is partially removed or disturbed, allowing coherent cellulose surfaces to become bonded, as in papermaking. Accompanying the removal of noncellulosic materials are the opposing dimensional changes of the two fiber components on mercerization, resulting in a "welding" of the primary wall to the fiber body.

The tendency of the fiber in mercerization to swell against the constriction of the primary wall apparently does not cause damage to the outer membrane in most fibers. However, it was observed that some fibers after removal of the reagent and drying, when given a second exposure to 18% NaOH, showed extensive splitting and peeling of the primary wall. The amount of tearing was reduced when the fibers were held at constant length during the treatment. Since the perimeter of fibers is reduced by mercerization and drying, an observation consonant with the transverse shrinkage of the primary wall, the splitting of the wall on subsequent swelling may occur because the wall is stretched to a greater extent on reswelling. In the case of coarse Asiatic cottons, splitting of the primary wall often occurred on the first exposure to the 18% alkali, and holding the fibers at constant length did not decrease the frequency of this phenomenon.

Exposure to Acid Hydrolytic Conditions

Cotton fibers exposed to aqueous mineral acids disintegrate, the extent depending upon temperature and period of exposure. The phenomenon of disintegration is probably initiated and caused by the cleavage of primary valence bonds in the cellulose chains. As Hock [6] and others have shown, the process culminates in the formation of small fragments consisting of aggregates of minute elongated bodies about 150 angstrom units or less in diameter. In the case of an extremely thin membrane like the primary wall, rapid disintegration of the original structure would be expected. However, sleeves of the unpurified wall, as well as those given preliminary purification to remove wax, etc., showed surprising resistance to disintegration when treated with 6*N* HCl at 100°C. Up to periods exceeding 6 hrs. under these conditions, the primary wall retained its sleeve-like form, and electron microscopy showed the fibrillar pattern of the purified material to be undisturbed. Short lengths of fibers subjected to this treatment showed marked decrease in length and width to an average of about 50% of their original size. Figure 13 shows a purified sleeve of primary wall after exposure to 6*N* acid for 4 hrs. at 100°C. The fibril systems of the wall are particularly clear in this micrograph. After 10 hrs. of hydrolysis under the conditions mentioned, some disintegration was observable, and after 16 hrs. no material having recognizable fibrillar texture was present. Even after 6 hrs. of hydrolysis, the wall exhibited sufficient strength to be manipulated through the operations of mounting for observation without breaking. Since it is improbable that the cellulose of the primary wall is chemically different from that of the remainder of the fiber, an explanation of its resistance to disintegration may lie in the woven arrangement and relatively long length of the fibrils composing it. Kling and Mahl [9] in their study of fiber surfaces observed that a hydrolytic treatment followed by alkaline kiering resulted in severe damage to the primary wall. In the present study of primary wall isolated from the fiber some disintegration was evident in specimens kiered after exposure to 6*N* HCl for 4 hrs. at 100°C, but many of the fragments retained their original sleeve-like

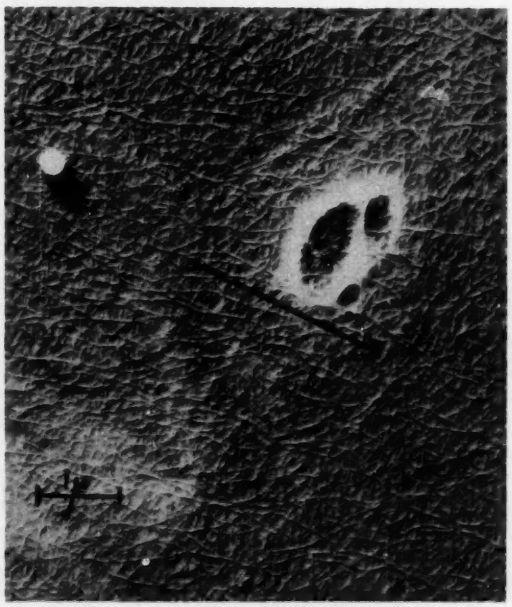


FIG. 13. *Electron micrograph of sleeve of primary wall treated with 6N HCl for 4 hrs. at 100°C after prior removal of noncellulosic material. Palladium shadowing.*

shape when examined under the microscope. The difference in results may lie in the fact that the wall is placed under some stresses when attached to the body of the fiber which are not operative in the isolated state.

Exposure to Dry Heat

No suitable method for exposing isolated fragments of primary wall to dry heat for extended periods of time was found that would allow subsequent examination in the electron microscope. Accordingly, an effort was made to remove the primary wall from heated fibers by the wet beating technique. It was found that heating made the primary wall progressively more difficult to remove in this manner, but small fragments were thus isolated for observation. Moderate heating (80° to 90°C for 2 to 3 hrs.) did not seem to change the appearance of the wall, although these temperatures are high enough to melt the cotton wax. It must be noted in this connection that the temperature rise of specimens exposed to the electron beam during examination in the electron microscope is 75° to 100°C [5] or even more. Heating at higher temperatures for longer periods caused the primary wall to assume a brownish color, and in contrast to the flat sheets or sleeves of untreated material, these specimens exhibited a ruffled appearance. Figure 14 shows a fragment of the wall beaten off of a fiber heated at 160°C for 16 hrs. In appearance it resembles the surface of a fiber such as is shown in Figure 2. The effect on the waxes of heating may parallel the oxidative "setting" of unsaturated hydrocarbon chains in paint film; or a polymerization of the waxes and other substances present in the wall (in some unknown manner) may cause the stiffness of the heated membrane.

FIG. 14. *Electron micrograph of fragment of primary wall beaten off fiber heated at 160°C for 16 hrs. Chromium shadowing.*

General Considerations

The results of the experiments reported here are undoubtedly subject to a large "sampling error" inherent in all forms of microscopy. Generalizations based on observations of so limited a portion of the whole fiber surface or outer membrane may be only remotely related to actual conditions present in bulk operations. The micrographs illustrating the primary wall in each of the conditions studied were chosen to represent the typical appearance of the treated specimen. In general, dozens of fields of specimens prepared in duplicate or triplicate experiments were examined before photography was carried out. Perhaps a more serious objection to the validity of the observations, with respect to actual processing conditions, is that the behavior of the primary wall *in situ* may be at variance with its reaction when isolated from the fiber. Insofar as the experimental conditions were similar, however, the observations reported here are in general agreement with those of Kling and Mahl [8, 10] whose studies were made on fiber surface replicas. It is thus reasonable to assume that the ultrastructure of the primary wall and its behavior in the various environments differ only in degree from the descriptions given here.

From a technological point of view, the topography and structure of the primary wall can be considered to impart certain gross properties to the cotton fiber. The surface rugosities of the whole fiber, while probably too small to make an important contribution to the frictional forces between fibers, are nevertheless capable of engaging and mechanically holding particulate matter, such as is present in some types of soil. The presence of wax on the surface of the fiber, however, is known to affect the frictional properties of cotton. The function of the outer wall as a water-resistant covering is apparent, as its surface does not appear to have naturally occurring pores, and the hydrophobic nature of the

wax present in the membrane makes it an effective barrier to the passage of aqueous solutions. Once the noncellulosic matrix is disturbed or removed, however, the interfibrillar spaces of the cellulose network are large enough to permit penetration of relatively large molecular aggregates; under these conditions, the adsorption of large molecules of dyes, resins, etc., must be governed by the structure of the secondary thickening of the fiber. The tendency of the primary wall to shrink on exposure to mercerizing caustic, thus opposing the swelling of the fiber body, is a contributing factor in the shape change and smoothing of the fiber and its surface by this process. The persistence of the cellulosic framework of the wall, with its complicated arrangement, through the operations of alkaline kiering and acid hydrolysis, indicates that its function as a limiting member of the fiber in swelling media must continue to be taken into account.

If complete removal of the noncellulose materials present in the wall is to be accomplished by alkaline kier, the period of kiering with the more dilute caustic solutions must be extended to 6 hrs. or more. While the effect on the ultimate utility of the fiber or fabric of primary wall damage during kiering has not yet been evaluated, it is reasonable to assume that the bulk of the fiber would also suffer attack when this occurs; avoidance of damage to the outer wall in fiber purification would allow the desirable properties of the membrane to contribute to the useful behavior of the textile structure. Peroxide bleaching, without prior kiering of the cotton, seems to remove effectively the materials which cover the cellulose framework of the primary wall. Whether this treatment alone gives satisfactory bleaching on a commercial scale is not known definitely.

A consideration of the fabric-like structure of the cellulose fibrils of the primary wall leads to speculation on the nature of the growth process responsible for such a complex architecture. While it is improbable that the enigma of cell wall morphogenesis can be solved by microscopy, the realization of the complexity of the physical structure dealt with is useful in interpreting the observations of commercial practice and utilization.

Acknowledgment

The authors are grateful to Tulane University Biophysics Department and Charity Hospital, New Orleans, La., for permission to use the electron microscope; and to Ruth Giuffria and Ines V. deGruy for assistance in the preparation of the manuscript.

Literature Cited

1. Anderson, D. B., and Kerr, T., *Ind. Eng. Chem.* **30**, 48–54 (1938).
2. Berkley, E. E., *Am. J. Botany* **29**, 416–23 (1942).
3. Frey-Wyssling, A., "Submicroscopic Morphology of Protoplasm," 2nd English ed., New York, Elsevier Publishing Co., 1953.
4. Goldthwait, C. F., and Guthrie, J. D., "Chemical Properties of Cotton Fiber," in Matthews' Textile Fibers, 6th ed. (H. R. Mauersberger, editor), New York, John Wiley & Sons, Inc., 1954, pp. 219–56.
5. Hall, C. E., "Introduction to Electron Microscopy," New York, McGraw-Hill Book Co., Inc., 1953.
6. Hock, C. W., TEXTILE RESEARCH JOURNAL **20**, 141–51 (1950).
7. Kettering, J. H., and Kraemer, R. M., *Am. Dyestuff Reptr.* **35**, 285–7 (1946).
8. Kling, W., and Mahl, H., *Melliand Textilber.* **31**, 407–13 (1950).
9. Kling, W., and Mahl, H., *Melliand Textilber.* **32**, 131–6 (1951).
10. Kling, W., and Mahl, H., *Melliand Textilber.* **33**, 829–32 (1952).
11. Marsh, J. T., "Mercerising," London, Chapman and Hall, 1941.
12. Marsh, J. T., "An Introduction to Textile Bleaching," London, Chapman and Hall, 1946.
13. Moore, A. T., *Stain Technol.* **28**, 149–54 (1953).
14. Mühlethaler, K., *Biochim. et Biophys. Acta* **3**, 15–25 (1949).
15. O'Kelley, J. C., "Elongation of the Cotton Fiber," Doctoral thesis No. 1128, Iowa State College, Ames, Iowa, 1950; abstract in Iowa State College *J. Sci.* **26**, 258 (1952).
16. Orr, R. S., Humphreys, G. C., and Grant, J. N., TEXTILE RESEARCH JOURNAL **22**, 89–93 (1952).
17. Roelofsen, P. A., *Biochim. et Biophys. Acta* **7**, 43–53 (1951).
18. Rollins, M. L., *Anal. Chem.* **26**, 718–24 (1954).
19. Segal, L., Tripp, R. C., Tripp, V. W., and Conrad, C. M., *Anal. Chem.* **21**, 712–18 (1949).
20. Tripp, V. W., Conrad, C. M., and Mares, T., *J. Phys. Chem.* **56**, 693–6 (1952).
21. Tripp, V. W., Moore, A. T., and Rollins, M. L., TEXTILE RESEARCH JOURNAL **21**, 886–94 (1951).
22. Tripp, V. W., and Rollins, M. L., *Anal. Chem.* **24**, 1721–8 (1952).
23. Viktoroff, P. P., and Goldberg, B. B., *Melliand Textilber.* **12**, 638–41 (1931).
24. Whistler, R. L., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards* **24**, 555–65 (1940).

(Manuscript received June 17, 1954.)

Fine Structure in Viscose Fibers

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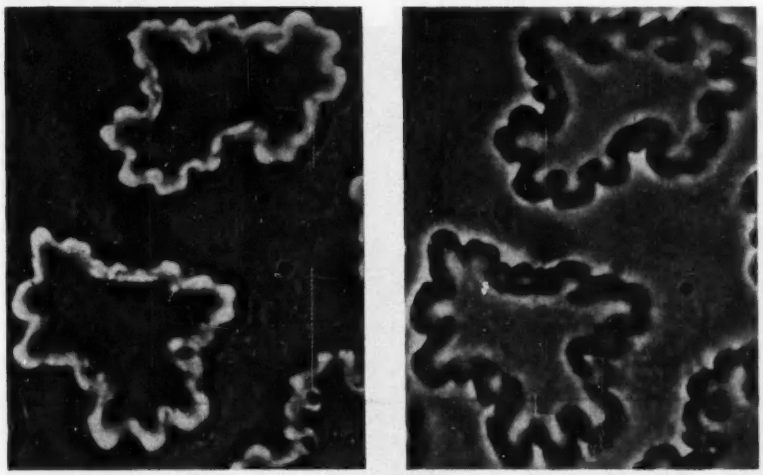
SINCE one of us first showed that viscose fibers have nonuniform structures [22], much work has been done to relate these to variations of axial orientation [1, 6, 13, 19, 21, 26, 31], transverse orientation [10, 26, 28], lateral order [15], swelling and permeability [16, 19, 24, 25], the retention of dyes and other substances [2, 3, 4, 8, 10, 12, 16, 19, 22, 28], and density [1, 5, 14]. In spite of the large amount of work which has been done, there are still disagreements between the deductions and even the observations made by different workers.

Further studies of these subjects have been made in these laboratories, and a number of new observations have been made which show that the structures present are often far more complicated than the old skin-and-core model.

A large number of fibers have been examined, some of which were specially spun, but since much of the new evidence is microscopical, it clarifies the presentation to consider a particular sample of fibers. The sample selected shows the new features very clearly, but similar structural details have been observed in many other fibers, and the methods used are generally applicable.

The viscose fibers described here were coagulated in a sulfuric acid, sodium sulfate, and zinc sulfate bath of high osmotic pressure, and they were rather less oriented than the normal viscose rayon used for textile purposes. They had an optical orientation factor of 0.35 [11], 35% crystallinity by moisture absorption and density measurements [18], and a volume swelling of 126% at 20°C [27].

The cross sections in Figures 1 and 2 show that the fibers have a very clearly marked skin of lower refractive index than the core for light vibrating transversely to the fiber axes. This agrees with findings that the skin is more highly oriented in the axial direction than the core [1, 6, 13, 19, 21, 22, 26, 31]; that is, it is more highly oriented in a direction normal to the plane of the photomicrographs. The significance of the change of structure at the inner boundary of the skin, which is seen in Figure 1, is supported by the phenomena recorded in Figure 2. These show that the inner Becke line between



a *b*

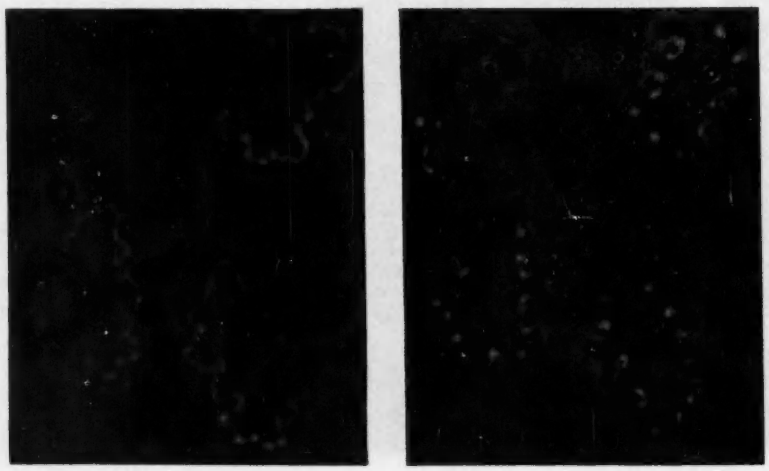
FIG. 1. *5-μ-thick viscose rayon sections mounted in ethyl salicylate* ($n_D = 1.523$), *examined by a 1.8-mm. oil-immersion objective, using a narrow cone of illumination.* a—*Microscope focused down.* b—*Microscope focused up.*

skin and core remains even when the outer Becke line between skin and mountant is extinguished by a suitable choice of wave length for the observations, depending on the greater dispersion of the mountant than of the fiber [7]. This gives strong support to the structural significance of the inner Becke line.

Figures 1 show indications of changes of refractive index within the skin itself, which appears to be far from a simple homogeneous structure. This deduction is supported by the appearance of the cross sections when examined by polarized light, as in Figures 3. When similar regions of any two of these are compared, it will be observed that there are marked local differences between the inner Becke lines and within the skin regions. Very marked changes occur at the inner faces of the cusps. It will be observed at a cusp that the light region extends further into the core when the plane of vibration is parallel to the axis of symmetry of the cusp. This indicates that there is some tangential orientation in the skin in the regions of the apices of the cusps. When the surface of the skin is nearly straight, the phenomenon is reversed. Here the bright region extends further inwards when the plane of polarization is parallel to the line of the periphery. This indicates that the orientation of the skin is radial in these regions, which is in agreement with the compressive process suggested by Preston and Narasimhan [26], and confirms the deductions of Hermans [10] from birefringence phenomena. At first this would appear to conflict with the hypothesis of Sisson and Morehead [29] that crimped viscose is produced by tension in the skin sufficient for it to split. The geometry of their cross sections shows that, if this happens as a primary process, at a subsequent stage the skin is compressed into serrations. It is clear that the skin structure in the cusps and lobes is complicated by the effect of folding, which superposes stretching on the outside of a bend on general compression. The layer of core lying next to the skin shows dark spots in Figure 3 wherever the plane of polarization is parallel to the skin, which indicates the presence of an inner skin with tangential orientation.

The phase-contrast observations shown in Figures 4 and 5 confirm the general findings obtained using the Becke method. The phase-contrast photomicrographs taken with polarized light confirm the complex structure of the skin. If Figures 5a and b are compared, it will be seen that there is greater retardation in the linear portions of the skin when the plane of polarization is normal to the general direction of the periphery, which indicates radial orientation. In the cusps the greater retardation is observed when the plane of polarization is tangential, which indicates tangential orientation in these regions.

In the core regions in Figure 4 the darkest parts are contiguous to the skin. The phenomenon is clarified by the observations given in Figures 5. Here it will be seen that the very dark regions are contiguous to the skin when it runs parallel to the plane of polarization. These observations are ex-



a *b*

FIG. 2. *5-μ-thick viscose sections, examined by a 1.8-mm. oil-immersion objective, using a narrow cone of illumination.* a—*Blue-green light,* $\lambda = 0.48\,\mu$; *microscope focused down.* b—*Yellow light,* $\lambda = 0.58\,\mu$; *microscope focused down.*

plicable if this region of the core possesses preferred tangential orientation. There is similarity in the location of the skin regions, which is shown by staining and by refractive index differences (see Figures 6).

The dichroic properties of the Sky Blue FF molecules and their adlineation to the cellulose molecules [17, 20, 23] indicate the orientations of the cellulose structures in the fibers in Figures 8. The clearly visible dichroism shows that the rectilinear segments of skin possess radial orientation, whereas in regions of high curvature of the skin, *e.g.*, near the apices of the cusps, the orientation is tangential. In water the sections are swollen to an extent that increases their linear dimensions by 50%, which is equivalent to a corresponding increase of resolving power and helps to distinguish fine details. A comparison of the double refraction patterns between crossed polarizers shows that there is no qualitative change of orientation produced by the water. A very thin unstained outer layer of the skin is more clearly seen in the swollen sections in Figure 9 than in the unswollen sections in Figure 7. The swollen sections when examined by polarized light, as in Figures 10, show

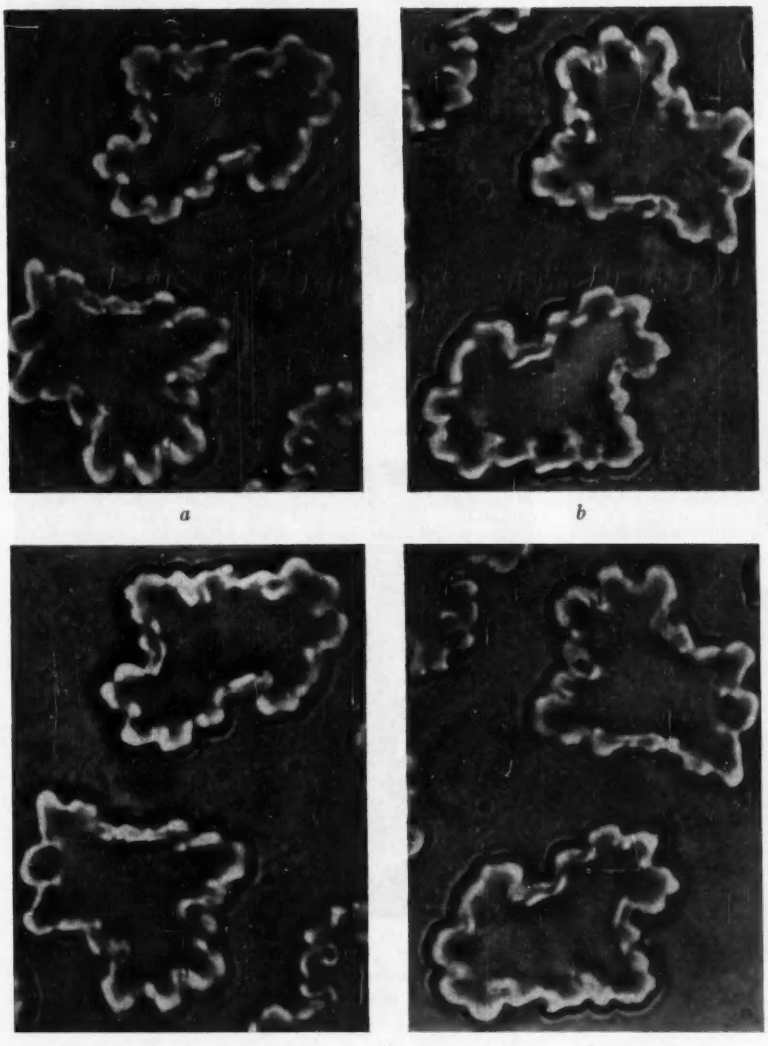


FIG. 3. *5-μ-thick viscose sections mounted in ethyl salicylate, examined by a 1.8-mm. oil-immersion objective, using a narrow cone of illumination. The planes of polarization are:* a—*N-S;* b—*NE-SW;* c—*E-W;* d—*NW-SE.*

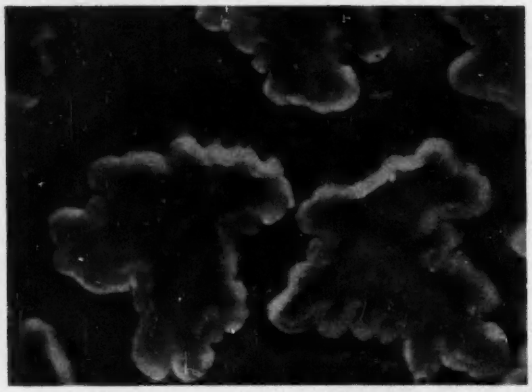
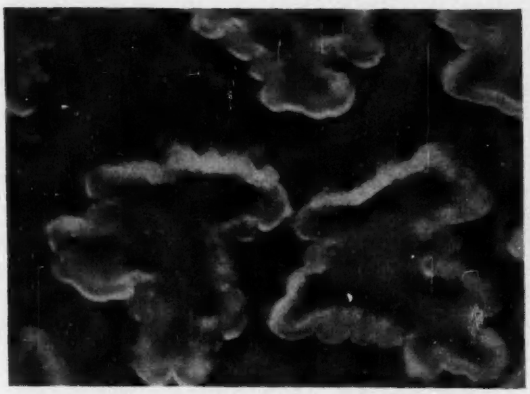


FIG. 4. *10-μ-thick viscose sections mounted in ethyl salicylate, examined by a 1.8-mm. oil-immersion phase-contract objective. The semiangle of the phase ring is 25° ± 2°.*

a

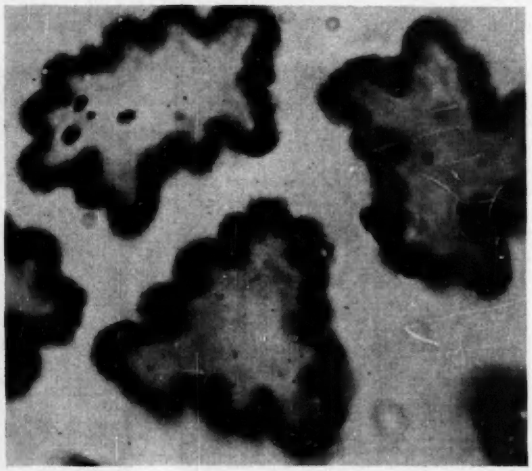


b

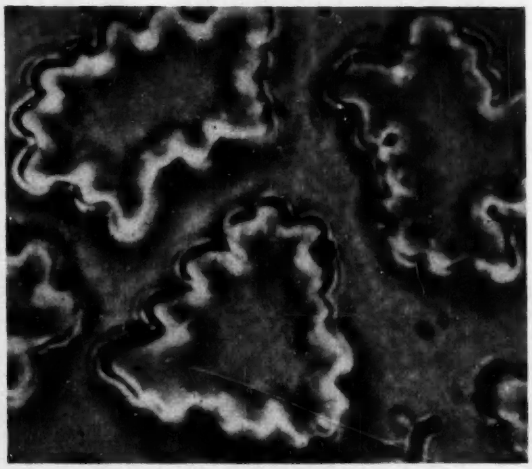
FIG. 5. *Same as Figure 4, except that plane-polarized light was used for the illumination. In* a, *the plane of polarization is N-S, and in* b *it is E-W.*

very marked dichroic phenomena. The straight segments of the second layer of the skin system show radial orientation, whereas the segments of high curvature show tangential orientation on the outsides of the curves and radial orientation on the insides of the curves. This confirms the deductions made from the Becke-line and phase-contrast observations.

Congo red (Figure 11) and Sky Blue FF staining showed a greater dye absorption in core than



a



b

FIG. 6. *5-μ-thick viscose sections. Skins stained with Victoria Blue, mounted in ethyl salicylate, and examined by a 1.8-mm. oil-immersion objective.* a—*Red light and full cone of illumination.* b—*Blue light and narrow cone of illumination.*

skin, which indicates a difference in swelling of these regions. Direct measurements of the comparative swelling of the skin and core confirmed this, but in the nature of things can only be of low accuracy. A more accurate method depends on the change of refractive index with moisture content [11]. When swollen, the core has a lower refractive index than the skin (Figure 13), which confirms that it swells more. The dichroism of the Congo red-stained sections (Figure 12) is interesting. Maximum absorption is shown when the plane of polarization is at right angles to the direction of maximum compression, indicated by the geometry of the cores of the sections.* Thus the dichroism in a lobe of a section is positive in the direction of its maximum extension. Similarly, in an elongated section the maximum absorption is in the direction of maximum extension. These dichroic phenomena indicate that there are preferred orientations in the core which lie normal to the direction of compression.

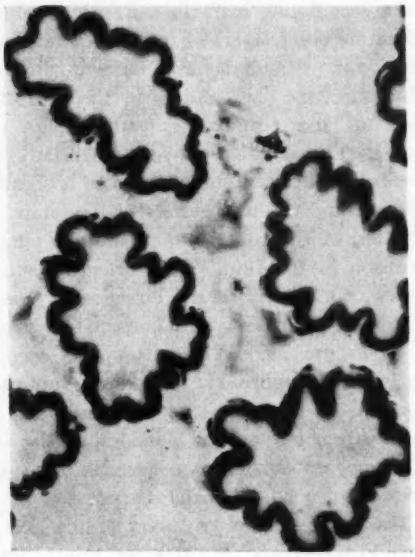
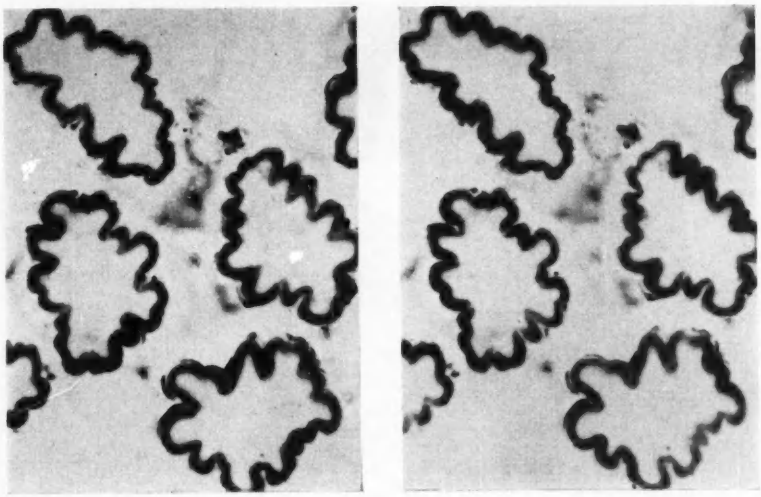


FIG. 7. *4-μ-thick sections of viscose dyed with Sky Blue FF (C.I. No. 518) at 80°C after mounting on slide; partially stripped with 13% pyridine solution for 2–4 min.; mounted in ethyl salicylate and examined with a 1.8-mm. oil-immersion objective using 3/4 cone illumination.*

As the different transverse orientations in different parts of the cross sections must be caused by the processes of extrusion and coagulation, as originally discussed by Sisson [28], it is important to consider these processes in some detail. The first process to consider is the extrusion through the spinneret aperture. Under the usual conditions of manufacture the relaxation time of the oriented macromolecules in the viscose is of the order of a millisecond [9], and during this time the fiber travels about 1 mm. into the coagulating bath. Only a thin outer layer of the viscose filament can be penetrated during this

* Since all sections start with a circular shape, there must have been the greatest compression in the direction of the minimum diameters in the final sections.



a b

FIG. 8. *The same sections as shown in Figure 7 illuminated by plane-polarized light.* a—*The plane is NW-SE;* b—*The plane is NE-SW.*

short contact, with the coagulation bath. This probably accounts for the existence of the very thin outer layer, which is seen in Figures 9 and 10 and also in Figures 4 and 5.

The very thin unstained outer layer in Figures 10 is seen best in the regions where the skin folds so that two lobes make contact. Here there is a double thickness of the thin outer skin, free from the refraction and diffraction effects associated with the cellulose/water interface. This thin skin was shown by Ohara by metachromatic staining [2].

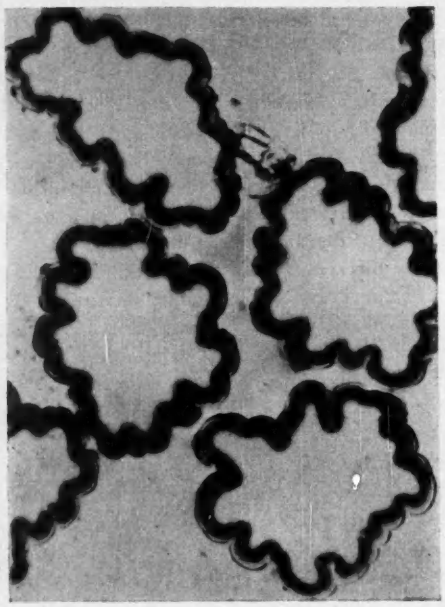
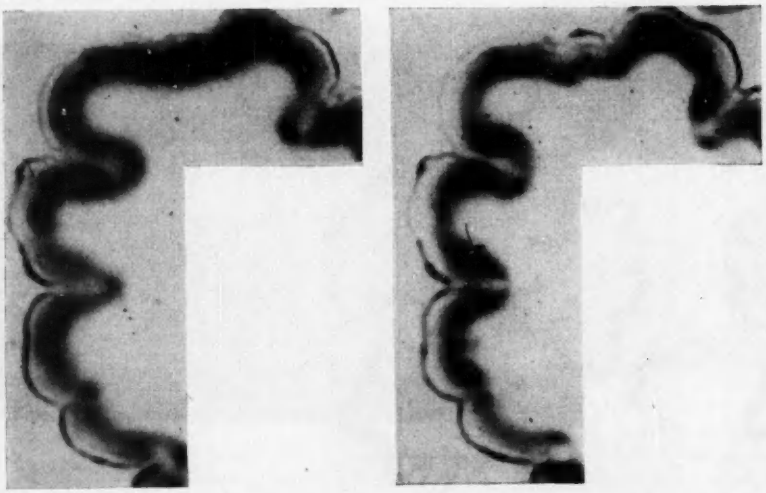


FIG. 9. *Same as Figure 7, except that the sections were mounted in water.* (×1180.)

In the coagulating bath the salts diffuse into and coagulate the outer layers of the fiber while the core is still liquid. Simultaneously there is progressive dehydration of the fiber, caused by the high osmotic pressure of the coagulating bath. This causes shrinkage. Considerable dehydration occurs in the skin before the dehydration of the core is significant.

Subsequently, the main effect on the skin of the dehydration of the core is to promote a tangential compression of the skin. This orients the macromolecules transversely to the direction of compression [26] and produces a radial orientation as shown by *A* in Figure 14. When crumpling occurs, as shown by *B* in Figure 14, the skin is subjected to compression on the insides of the bends and a superposed stretching on the outsides of the bends, which compensates or even exceeds the general compression, depending on the sharpness of the folding. The inner and outer layers of the skin at a lobe should show opposite preferred orientations; at a cusp, where the curvature is greater, the effect should be even more pronounced. These orientations are tangential on the outside of a bend and radial on the inside, as is seen very clearly in Figures 5 and 10.



a *b*

FIG. 10. *Same as Figure 9, except that polarized light was used for illumination.* a—*The plane is N-S;* b—*The plane is E-W.*

These orienting effects of compression show up clearly when applied to a random structure. They can have little effect on the outermost very highly axially oriented structure.

In addition to the compressive effects caused in the skin by shrinkage of the core, the formation of a lobe must also compress the core locally and produce a preferred orientation parallel to the axis of symmetry of the lobe, which is perpendicular to the direction of compression, as indicated in Figure 15. This again agrees with the experimental observations shown, for example, in Figures 12.

As the volume of the fiber decreases during formation, the skin must move inwards under the transitory osmotic-pressure difference between coagulating bath and fiber. This inward movement of the skin is equivalent to a compression, and should produce tangential orientation immediately contiguous to the skin. This is seen in Figures 3 and 5.

At the end of the investigations the results of which have been described, a Baker interference microscope [30] became available. This instrument measures the refractive indices of small regions of microscopical specimens. Viscose sections similar to those described above were examined with it. The thin outermost layers showed no double refraction; the second layers showed double refractions of 0.003

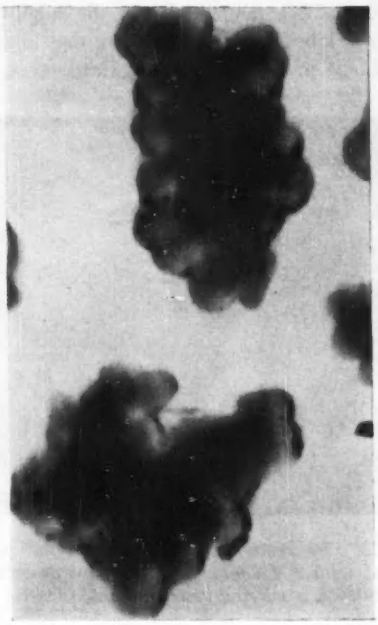
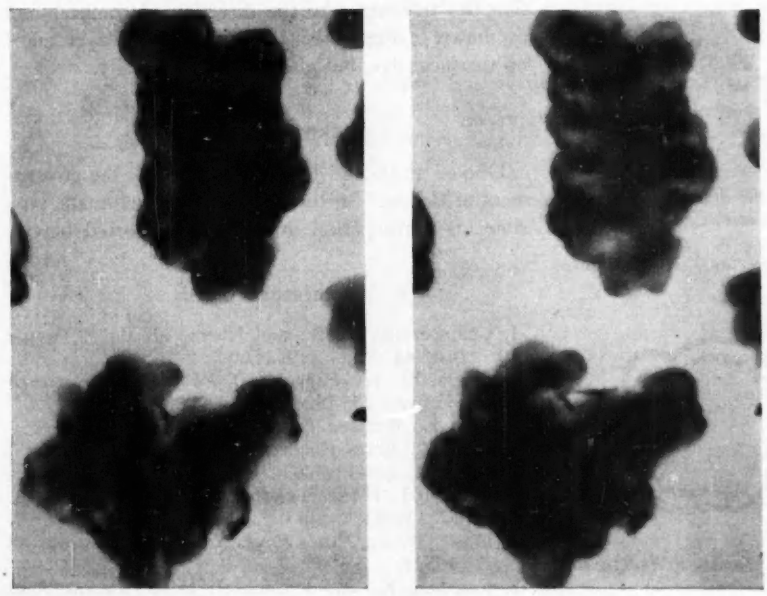


FIG. 11. *5-μ-sections of viscose dyed in 1% Congo Red (C.I. No. 370) for 1 hr. at room temperature. After washing in water and drying they were mounted in ethyl salicylate and examined by a 1.8-mm. oil-immersion objective using a 3/4 cone illumination.*



a *b*

FIG. 12. *Same as Figure 11, except that the illumination was plane-polarized light.* a—*The plane is N-S.* b—*The plane is E-W.*

to 0.005 positive tangentially in the highly curved portions of lobes and radially where the skin was approximately straight. The thin third layer showed a positive tangential double refraction of 0.001 to 0.002. The cores of lobes showed double refractions of 0.003 to 0.005 positive in the direction of extension of the lobes.

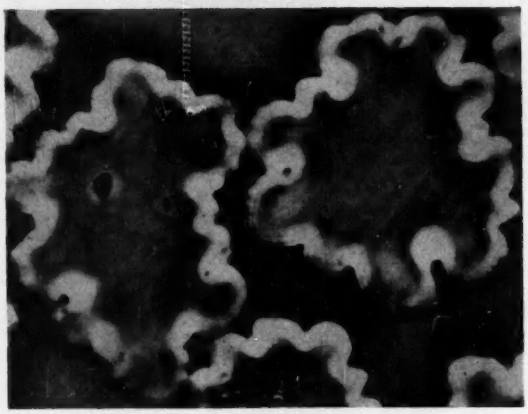


FIG. 13. *5-μ sections of viscose mounted in water, examined with a 1.8-mm. oil-immersion objective, and illumined with a narrow cone of light, focused up.*

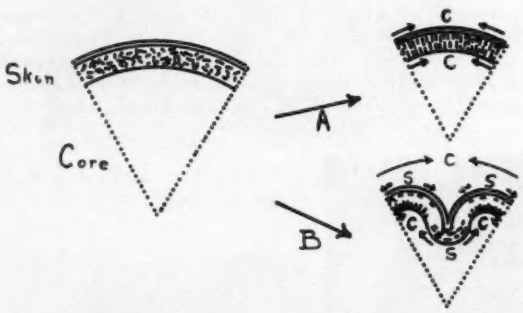


FIG. 14. *Effect on the skin of the dehydration of the core.* Left—*early stage of coagulations.* Right—*later stage of coagulation.* c—*Compression.* s—*Stretching.* |||—*Predominant transverse orientation.* A *and* B *are explained in the text.*

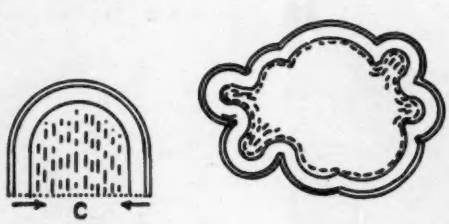


FIG. 15. *Local compression of the core, due to the formation of a lobe.*

FIG. 16. *Tangential orientation of third layer.*

There are apparently four distinct zones in a viscose fiber cross section. There is a very thin outer zone which appears not to dye and has no double refraction (in cross section). Within this thin outermost layer there is a second layer, the so-called "skin," some of the properties of which have been described previously but which is now demonstrated to have both radial and tangential orientations, as shown in Figure 14. The orientation in any particular position depends upon whether the general compression or the folding effects predominate. The second layer takes up less dye than the core, but retains it firmly.

The third layer is thin but not sharply defined on the core side and shows tangential orientation irrespective of the degree of folding, as indicated in Figure 16. This layer has dyeing characteristics different from those of the second layer of the skin and of the core. It absorbs more dye than the skin, but strips more easily than the skin and less easily than the core.

The innermost region of the fiber shows orientation conditioned by the deviation of the fiber shape from circularity. The direction of preferred orientation lies transverse to the direction of compression, as shown in Figure 15. This innermost layer takes up the most dye, but also strips most easily.

Acknowledgment

One of us (G. D. J.) wishes to thank the government of Bombay for the scholarship which made possible his participation in the work reported herein.

Literature Cited

1. Chamberlain, N. H., and Khera, M. P., *J. Textile Inst.* **43**, T123 (1952).
2. Ohara, K., *Sci. Papers Inst. Phys. Chem. Research (Tokyo)* **25**, 152 (1934).
3. Elöd, E., *Melliand Textilber.* **34**, 1 (1953).
4. Elöd, E., *Textil-Rundschau* **9**, 13 (1954).
5. Elöd, E., and Frohlich, H. G., *Melliand Textilber.* **27**, 103 (1946); TEXTILE RESEARCH JOURNAL **18**, 487 (1948).
6. Faust, R. C., *Proc. Phys. Soc. (London)* **65**, 48 (1952).
7. Freeman, K., and Preston, J. M., *J. Textile Inst.* **34**, T19 (1943).

8. Frey-Wyssling, A., *J. Polymer Sci.* **2**, 314 (1947).
9. Gonsalves, V. E., *Proc. Intern. Rheol. Congr.* **II**, 239; **III**, 66 (1948).
10. Hermans, P. H., *XIth Intern. Congr. Pure Applied Chem.* **5**, 85 (1947).
11. Hermans, P. H., "Contributions to the Physics of Cellulose Fibres," Amsterdam, Netherlands, Elsevier-Publishing Co., Inc., 1946, 115ff.
12. Hermans, P. H., TEXTILE RESEARCH JOURNAL **18**, 9 (1948).
13. Hermans, P. H., TEXTILE RESEARCH JOURNAL **20**, 553 (1950).
14. Hermans, P. H., *Kolloid-Z.* **122**, 1 (1951).
15. Ingersoll, H. G., *J. Appl. Phys.* **17**, 924 (1946).
16. Landells, G., Mhatre, S. H., and Narasimhan, K. I., *J. Textile Inst.* **39**, T148 (1948).
17. Marshall, W. J., and Peters, R. H., *J. Soc. Dyers Colourists* **62**, 271 (1947).
18. Mhatre, S. H., and Preston, J. M., *XIth Intern. Congr. Pure Applied Chem.* **5**, 161 (1947).
19. Morehead, F. F., and Sisson, W. A., TEXTILE RESEARCH JOURNAL **15**, 443 (1945).
20. Morton, T. H., *J. Soc. Dyers Colourists* **62**, 271 (1946).
21. Okajima, S., Hayama, S., and Kobayashi, K., *Bull. Chem. Soc. Japan* **25**, 3 (1952).
22. Preston, J. M., *J. Soc. Chem. Ind.* **50**, 199T (1931).
23. Preston, J. M., *J. Soc. Dyers Colourists* **47**, 312 (1931).
24. Preston, J. M., Trans. Faraday Soc. **42B**, 131 (1946).
25. Preston, J. M., and Bhat, R. V., *J. Textile Inst.* **39**, T211 (1948).
26. Preston, J. M., and Narasimhan, K. I., *J. Textile Inst.* **40**, T327 (1949).
27. Preston, J. M., Nimkar, M. V., and Gundavda, S. P., *J. Textile Inst.* **42**, T79 (1951).
28. Sisson, W. A., *J. Phys. Chem.* **44**, 513 (1940).
29. Sisson, W. A., and Morehead, F. F., TEXTILE RESEARCH JOURNAL **23**, 152 (1953).
30. Smith, F. H., Brit. Patent 639,014 (June 21, 1950); U. S. Patent 2,601,175.
31. Wuhrman, K., *Helv. Chim. Acta* **28**, 666 (1945).

(Manuscript received February 23, 1953; revised manuscript received August 3, 1954.)

Correction

The following errata appeared in "The Nature of the Hemicelluloses of Jute Fiber, Part II," by P. C. Das Gupta and P. B. Sarkar, in the August 1954 issue:

Page 709. In Structure III, H, OH should be substituted for H_2OH.

Page 710. In the structural formula at the upper left, H—OH should be added to the blank corner of the central xylose unit. At the extreme right, 4 should be substituted for H after the end xylose unit and last bracket.

Abrasion Resistance of Multifilament and Staple Yarns Tested on Modified Walker Abrader*

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Southern Research Institute, Birmingham, Alabama

Abstract

Nine multifilament yarns and 18 staple yarns were tested on a modified Walker Abrader using the same low tension for all yarns. To correct all filament yarns to the same fineness (100 den.), multiple strands of filament viscose 100/40 were tested, and a correction factor was obtained. In the same manner, multiple strands of Kuralon 80/2 were tested to obtain a correction factor for staple yarns. The Walker Abrader results for staple yarns were also corrected to 100 den.

After the results had been corrected, acetate filament yarn was found to have the lowest abrasion resistance and nylon filament yarn the highest abrasion resistance among the filament yarns. In the staple yarns, acetate 20/1 had the lowest abrasion resistance, and Dacron 60/2 (worsted) had the highest abrasion resistance. Comparing staple and filament yarns, acetate staple 20/1 had the lowest abrasion resistance, and nylon 100/40/2.5 filament had the highest abrasion resistance.

In general, the abrasion resistance of filament yarns was greater than the abrasion resistance of staple yarns.

THE present work was inspired by a paper given by Dr. George Susich at the New Orleans meeting of The Fiber Society [2]. At that time Dr. Susich talked about the flex abrasion of textile fibers. He pointed out that there was no published information on the abrasion of yarns, although there was an abundance of information on the abrasion of fabrics. This information is not necessarily usable because the data are influenced by form factors such as thickness, structure of filling yarns, and the inherent abrasive behavior of the fiber material itself. Susich emphasized the fact that in order to learn about the abrasive behavior of yarns, one must test yarns alone to minimize the influence of other factors. For this reason, Susich tested bundles of yarns on the Stoll-Quartermaster Abrasion Tester. He varied the abrading action by changing both the yarn pressure and tension. Bundles of yarn were flex abraded by a square-edged steel bar until rupture occurred. Instead of comparing cycle numbers at break, Susich compared the loss of grex of the yarns abraded under similar abrasive action. His results were expressed as "relative abrasion damage," and were correlated to that of nylon type 300 multifilaments. He found nylon to have the lowest abrasive damage of the materials tested.

In his paper Susich mentioned the Walker Abrader, and suggested that its usefulness had not been fully appreciated. Inasmuch as we at Southern Research Institute have used this instrument almost daily for the last 8 years in the evaluation of sizes on warp yarns, it was suggested that we undertake to repeat Susich's work using the Walker Abrader. Dr. Susich kindly supplied all the yarns that are described in his paper.

Because of the nature of the operation of the Walker Abrader, it was not possible to obtain results for two of the yarns, namely, Thermovyl 30/1 and Dynel 20/1. These yarns have unusually high elongation, and the tension bars of the Walker Abrader actuate the cut-off mechanism after only one or two abrasion cycles.

It should be pointed out that the abrasive damage produced by the Stoll-Quartermaster Abrader is caused by contact of yarns with a sharp metallic object. In the case of the Walker Abrader, the main abrasive damage is produced by rubbing the yarn against itself. To be sure, a slight portion of the damage is probably caused by rubbing around the central pin.

* Presented as a contribution from the Textile Section of Southern Research Institute at the Fall Meeting of The Fiber Society at McGill University, Montreal, Canada, Sept. 14, 1954.

† Head, Textile Section.

‡ Associate Physicist, Textile Section.

Procedure

The Walker Abrader [3], as shown in Figure 1, was used to measure the abrasion resistance of the various yarns. The individual strands of yarn are attached to the top frame by stationary clamp *A* and on the bottom by clamp *B*, which is attached to the lever arm *J*. The mid-portion of each strand is trained about staggered pins *F*, which are mounted on a movable plate *E*, as shown in Figure 2. The movable plate *E* may be shifted to give the desired angle (the angle that the upper and lower pins make with the center pin). The angle used in this experiment was 106°. The length of the stroke is also adjustable, and in this case the stroke length was 1.5 in.

A loop is made about the middle pin (see Figure 2) so that there is a crossover at a sharp bend. A "downward" loop was used for Z-twist yarns, and an "upward" loop was used for S-twist yarns. If the loop on the pins is not in the same direction as the twist of the yarn, the number of cycles required for breaking will be much lower because of the "opening" effect on the twist of the yarn.

As the plate holding these pins moves up and down in an arc, actuated by a motor-driven cam, the yarn is rubbed upon itself, and wear occurs in the sharp bend. The lever arms have adjustable weights *D*, so that varying tensions may be applied, depending on the types and sizes of the yarn under test. A counter *C* is connected to the abrader to indicate the number of cycles. When a yarn breaks, the back of the lever arm strikes the knock-off motion bar *G*, causing a microswitch to break the electric circuit. Thus the machine stops automatically after each yarn break. The machine is started again by adjusting the movable detent *H* to hold the lever arm. The only purpose served by these tension weights is to keep the yarn from riding up on the upstroke. Thus only enough tension to overcome this effect is necessary. However, certain yarns that have high resistance to abrasion would require inordinately long periods for each test if the minimum weight were used. In these cases it is the practice to use a heavier weight to hasten the rupture of the yarns. However, this is valid only when a given type of yarn is compared with a similar yarn that has been modified in some way, such as a sized warp yarn compared to the unsized yarn.

In connection with the present investigation it became necessary to modify the Abrader as originally designed by Walker and Olmstead [3]. It was important to select a tension weight that would be satisfactory for all the yarns to be tested because of the requirement of direct comparison of the abrasive action of the yarns upon themselves. Thus, when a weight which was suitable for a rapid test for nylon yarn was used—the 100-g. weight—the cellulose acetate yarns broke quickly under the excessive tension. The different positions on the lever arms are shown in Figure 3. The tension at position *S*, where the

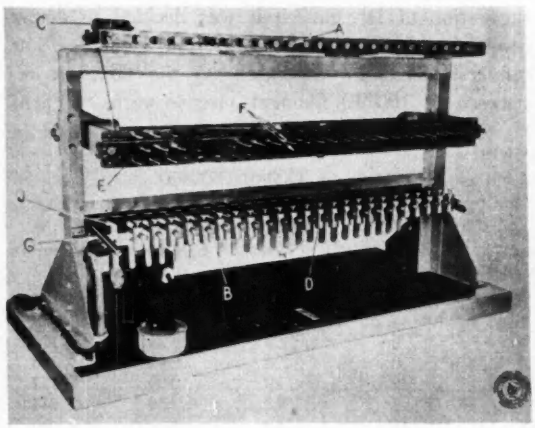

FIG. 1. *Walker Yarn Abrader.* A, *top clamp;* B, *bottom clamp;* C, *counter;* D, *adjustable weights;* E, *movable plate;* F, *pins;* G, *knock-off motion;* H, *movable plates to hold lever arm off stop motion;* J, *lever arm.*

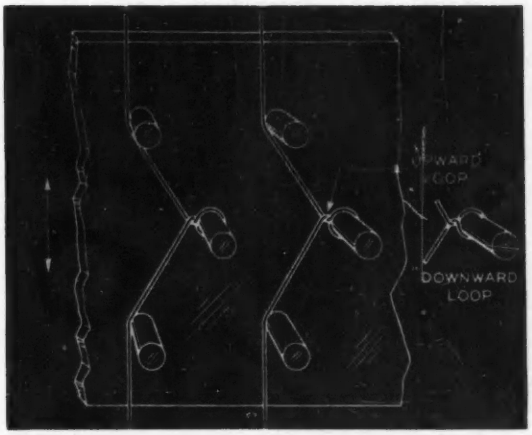

FIG. 2. *Movable plate with staggered pins showing method of mounting S- and Z-twist yarns.*

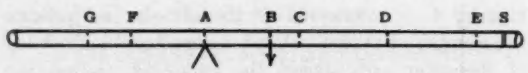

FIG. 3. *Walker Abrader lever arm, showing various weight positions.* A, *fulcrum (fixed point of rotation);* B, *center of gravity (point where rod balances);* C, *position of weight—marked on machine as 50 g.;* D, *position of weight—marked on machine as 75 g.;* E, *position of weight—marked on machine as 100 g.;* S, *place where yarn is attached;* F, *weight position* I; G, *weight position* II.

lower end of the yarn is attached, has been measured for all positions of the adjustable weight *D*, as shown in Figure 1. These measurements do not agree with the engraved weights on the machine. Because of our requirement for lower tensions than those provided by the Walker Abrader as received, the tensions provided by the lever with weights removed and with weights in two counter positions have also been determined. These values are as follows:

Position of weight (see Figure 3)	Weight indicated on machine	Calculated tension on yarn (g.)
E	100-g. position	63.5
D	75-g. position	51.3
C	50-g. position	39.0
Weight removed		26.0
F	counterposition *I*	15.9
G	counterposition *II*	9.8

In order to determine the tension-weight position which would give reasonable results with most of the yarns, and at the same time permit the inclusion of the yarns at either extreme (presumably cellulose acetate and nylon), it was necessary to experiment with various tension weights. In this respect, it should be pointed out that it is desirable to have the first break come at 10 or more cycles.

Strands from each of the filament yarns were tested on the machine with the weights in various positions on the lever arm. The results of this test are given in Table I. Since the weight position *G*, 9.8 g. (see Figure 3), is the only position that gives acceptable values for filament acetate, all yarns were tested with the weight in position *G*.

The form factors such as fineness, twist, structure, length of single fibers, and even atmospheric conditions presumably affect the abrasion resistance of yarn [2]. To make the comparison ideal, the different yarns should have form factors which are as similar as possible. In our investigation, tests were made on the same modified Walker Abrader in an atmosphere of 70° ± 2°F and 65% ± 2%R.H., and by one operator. However, the yarns varied as to twist, ply, and fineness.

Results

Filament Yarns

The nine filament yarns that were tested are listed in Table I. Since all the filament yarns had a fineness of 100 den. except for H.T. Fortisan 90/120/3, casein 300/40, and Saran 200/12/5, it was decided to compare the abrasion resistance of all the yarns at the same fineness (100 den.). The problem, then, was to find a method of converting all the results to a given fineness, namely, 100 den. Upon the suggestion of Dr. Susich it was decided to derive conversion factors for the different deniers. The conversion factor was based on the abrasion resistance of 100/40 filament viscose yarns. Yarns

TABLE I. PRELIMINARY TEST TO DETERMINE SUITABLE POSITION OF TENSION WEIGHT

Filament yarn	Walker Abrader cycles to first break					
	100-g. Position	75-g. Position	50-g. Position	No weight	Position *F*	Position *G*
Acetate 100/40/2.5	0	0	0	0	1	28
Casein 300/40	1	1	1	34	129	381
Saran 200/12/5	0	0	0	3	24	108
Orlon 100/40*	0	0	0	4	92	303
H.T. Fortisan 90/120/3	1	1	2	29	109	177
Regular viscose 100/40	0	0	1	12	50	144
Silk S 1303 (100 den.)	9	12	51	143	—	—
Dacron 100/40†	18	55	191	671	—	—
Nylon, Type 300, 100/40/2.5	746	1081	1891	2692	—	—

* Acrylic fiber, Du Pout.
† Polyester fiber, Du Pont.

were tested in four series, using one strand, two strands, three strands, and four strands. This is a crude attempt to simulate 100-, 200-, 300-, and 400-den. yarns. No attempt was made to impart a twist to the yarn multiples. The yarn was placed on the twenty-four positions of the Walker Abrader, and testing proceeded in the usual manner. The first twelve consecutive breaks were recorded in one column. The remaining twelve yarns were discarded, and the Abrader was restrung with twenty-four additional strands. The test proceeded until four sets of twelve breaks had been recorded. The first breaks in each column were averaged, the second breaks in each column were averaged, etc., until a column of twelve averages (each average derived from four values) was obtained. The grand average of the forty-eight breaks was then calculated. These results for each simulated denier are given in Table II. The four grand averages were plotted against their corresponding deniers on semilogarithmic paper. The abrasion cycles were plotted on the Y axis (logarithmic axis), and the deniers were plotted on the uniformly spaced X axis. The points lay approximately in a straight line. This plot is shown in Figure 4.

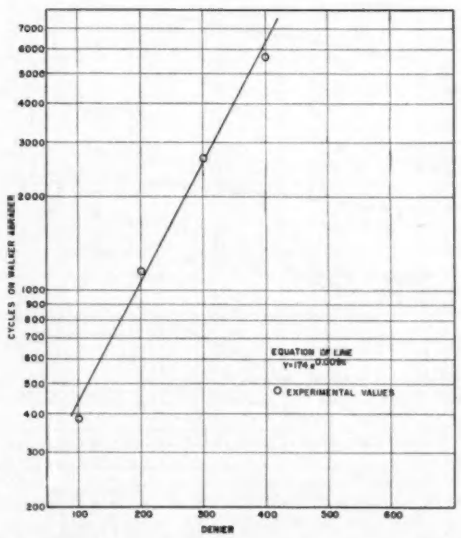

FIG. 4. *Effect of fineness of filament yarn on Walker Abrader cycles. Regular viscose 100/40 tested in multiples of one strand (100 den.), two strands (200 den.), three strands (300 den.), and four strands (400 den.).*

The equation for the curve was calculated to be

$$y = 174e^{0.009x},$$

where y = cycles on Walker Abrader and x = denier of yarn. The derivation of this equation is given in the Appendix.

The straight line in Figure 4 is a line calculated from the above equation. The points on the graph are the experimental results.

Assuming that the correction factor obtained for multifilament viscose rayon could also be used for other multifilament yarns, it became possible to correct the H. T. Fortisan, casein, and Saran results to 100 den.

To show how the correction factors were calculated, a 300-den. multifilament yarn will serve as an illustration:

$$\text{denier of yarn} = 300,$$
$$y = 174e^{0.009x};$$
$$\text{solving for } x = 100, \text{ then } y = 428;$$
$$\text{solving for } x = 300, \text{ then } y = 2579.$$

Now, in order to obtain a factor to convert the observed abrasion cycles for 300-den. yarn to the adjusted number of cycles for 100-den. yarn, the following derivation was made:

$$\text{factor} = \frac{428}{2579} = 0.166.$$

TABLE II. EFFECT OF FINENESS OF FILAMENT YARN ON ABRASION RESISTANCE (VISCOSE 100/40 TESTED IN MULTIPLES OF ONE, TWO, THREE, AND FOUR STRANDS)

Yarn break	Average Walker Abrader cycles to yarn break*			
	1 Strand (100 den.)	2 Strands (200 den.)	3 Strands (300 den.)	4 Strands (400 den.)
1	292	639	1,258	2,774
2	338	773	1,355	3,216
3	362	914	1,659	3,614
4	374	987	1,999	4,351
5	387	1,013	2,415	4,760
6	389	1,064	2,591	5,230
7	395	1,133	2,810	5,787
8	402	1,325	2,969	6,010
9	410	1,397	3,164	6,736
10	415	1,451	3,389	7,573
11	425	1,502	3,809	8,493
12	431	1,610	4,151	9,039
Grand average	385	1,151	2,631	5,632

* The figures opposite the numbers 1, 2, 3, 4, etc., are the averages of four breaks.

In Table III are listed the correction factors for all multifilament yarns of deniers other than 100 den.

In Table IV is given a list of the observed abrasion results before adjustment to 100 den. along with the results adjusted to 100 den. A frequency distribution was made, and the cumulative frequency was plotted for each filament yarn (see Figure 5).

Staple Yarns

The seventeen staple yarns that were tested are listed in Table V. The staple yarns were tested for abrasion resistance with the same tension (9.8 g.) that was used for the multifilament yarns. Inasmuch as there was no staple yarn of exactly 100 den., Kuralon 80/2, having a denier of 130, was tested in multiples of one, two, three, and four strands. This is a crude attempt to simulate 130-, 260-, 390-, and 520-den. yarns. The yarns were tested in the same manner as the filament yarns. These results are listed in Table VI. In this case, however, the four grand averages were plotted against the deniers on logarithmic paper rather than on semilogarithmic paper. The points lay approximately in a straight line. This plot is shown in Figure 6. At first an attempt was made to fit this data to an exponential curve like that for the filament yarns. However, a better fit was obtained using a power-function curve. The equation of the curve was calculated to be

$$y = 0.001x^{2.53},$$

TABLE III. CORRECTION FACTORS FOR MULTIFILAMENT YARNS

Yarn	Fineness of yarn (den.)	A (cycles calculated by formula)*	Factor to convert observed results to results adjusted to 100 den. $(428/A)$†
Casein 300/40	300	2,579	0.166
Saran 200/12/5	200	1,052	0.407
H.T. Fortisan 90/120/3	90	391	1.09
Regular viscose 100/40	100	428	1.0

* The theoretical number of cycles for each yarn was calculated from the formula $y = 174e^{0.008x}$, where x = denier of the yarn.

† The theoretical number of cycles for 100-den. yarn is 428.

TABLE IV. ABRASION RESISTANCE OF FILAMENT YARNS

Identification	Yarn fineness (den.)	Average cycles on modified Walker Abrader ($n = 48$) Observed results	Results adjusted to 100 den.*
Acetate 100/40/2.5	100	37	37
Casein 300/40	300	323	54
Saran 200/12/5	200	294	120
Orlon 100/40	100	310	310
H.T. Fortisan 90/120/3	90	295	322
Regular viscose 100/40	100	385	385
Silk S 1303 (100 den.)	100	720	720
Dacron 100/40	100	3,919	3,919
Nylon, type 300, 100/40/2.5	100	11,970	11,970

* These results were corrected to 100 den. using the factors obtained from Table III.

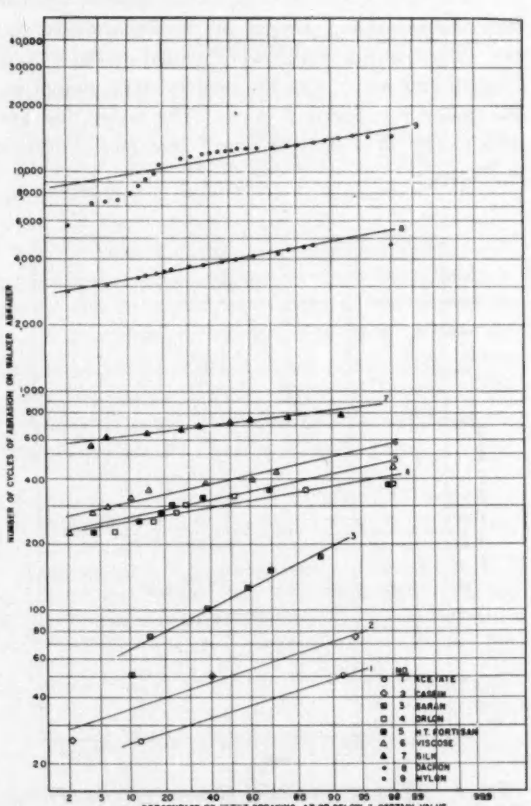

FIG. 5. *Abrasion resistance of multifilament yarns corrected to 100 den.*

where y = Walker Abrader cycles and x = denier. The derivation of this equation is given in the Appendix. The straight line in Figure 6 is a line calculated from the above equation. The points on the graph are the experimental results.

Assuming that the correction factor obtained for Kuralon 80/2 staple yarn could be used for other staple yarns, it then became possible to adjust the abrasion cycles of all the staple yarns to 100 den. However, it was necessary, in this case, to use the formula to calculate the theoretical cycles for 100-den. yarn. Then the factors listed in Table V were obtained in the same manner as the adjustment factors for multifilament yarns described previously.

In Table VII is presented a list of the observed abrasion results before adjustment to 100 den., along with the adjusted results. A frequency distribution was made, and the cumulative frequency of the adjusted values was plotted for each staple yarn (see Figure 7).

In Table VIII the abrasion-resistance results, adjusted to 100 den., for both multifilament and staple yarns are listed in order of increasing resistance to abrasion.

TABLE V. CORRECTION FACTORS FOR STAPLE YARNS

Yarn*	Fineness of yarn (den.)†	A (cycles calculated by formula)‡	Factor to convert observed results to results adjusted to 100 den. $(118/A)$§
Nylon 60/1	88	86	1.370
Dacron 20/1	266	1,400	0.084
Nylon 30/1	365	3,112	0.038
Dacron 60/2 (worsted)	278	1,565	0.075
Cotton 50/1	106	137	0.860
Fibravyl 75/1 (metric)	124	204	0.578
Untreated cotton 20/1	267	1,414	0.084
Wool 28.4/1 (worsted)	284	1,651	0.072
Kuralon 40/1	131	234	0.504
Kuralon 80/2	130	229	0.515
Wool 45/2 (metric)	410	4,169	0.028
Orlon 16/1	332	2,449	0.048
Orlon 15/1	352	2,839	0.042
Viscose 20/1	266	1,400	0.084
Decrystallized cotton 20/1	315	2,145	0.055
Acetate 20/1	266	1,400	0.084
Dacron 29/2	536	8,211	0.014
Theoretical yarn	100	118	1.000

* Unless otherwise indicated, the "cotton" numbering system is used.

† Although yarn size is generally expressed in denier for multifilaments and by the yarn number in cotton or worsted counts for staple yarns, all systems were converted to the denier system to permit direct comparison of yarn fineness for all the materials tested.

‡ The theoretical number of cycles for each yarn was calculated from the formula $y = 0.001x^{2.55}$, where x = denier of yarn, y = cycles.

§ The theoretical number of cycles for 100-den. yarn is 118.

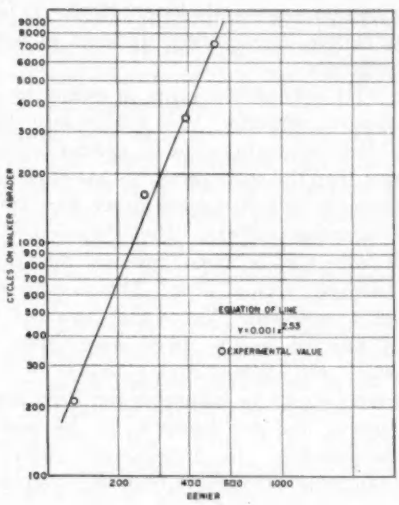

FIG. 6. *Effect of fineness of staple yarn on Walker Abrader cycles. Kuralon 80/2 tested in multiples of one strand (120 den.), two strands (260 den.), three strands (390 den.), and four strands (520 den.).*

TABLE VI. EFFECT OF FINENESS OF STAPLE YARN ON ABRASION RESISTANCE (KURALON 80/2, TESTED IN MULTIPLES OF ONE, TWO, THREE, AND FOUR STRANDS)

Yarn break	Average Walker Abrader cycles to yarn break* 1 Strand (130 den.)	2 Strands (260 den.)	3 Strands (390 den.)	4 Strands (520 den.)
1	136	1,056	2,299	5,404
2	156	1,327	2,622	5,730
3	162	1,352	2,731	6,220
4	175	1,500	3,041	6,766
5	189	1,587	3,254	6,955
6	196	1,655	3,470	7,098
7	221	1,730	3,502	7,546
8	233	1,781	3,694	7,976
9	249	1,857	3,779	8,108
10	260	1,859	3,979	8,287
11	269	1,895	4,113	8,447
12	278	1,957	4,372	8,849
Grand average	210	1,630	3,405	7,282

* The figures opposite the numbers 1, 2, 3, 4, etc., are the averages of four breaks.

Discussion

Table I shows the wide difference in results when acetate yarns and nylon yarns are tested, using the same tension. Very little tension is required with acetate yarn to obtain suitable results, whereas, when the same tension is used for nylon and Dacron yarns, the tests become excessively long. However, for the purposes of this investigation, duration of test has little significance.

Table VIII lists all the yarns in ascending order of resistance to abrasion. It is readily seen that, in general, filament yarns show a greater resistance to abrasion than the spun yarns. Some of the staple yarns seemed to be pulled apart rather than damaged by actual abrasion of fibers. Thus the effect of twist in staple yarns may be more important than the difference between types of fiber. This is a point that should be investigated. Yarns that appeared to be adversely affected by low twist were Orlon 16/1 (Champlain) and Dacron 20/1 (Dixie).

The curves drawn in Figures 5 and 7 are not calculated curves, but are drawn to fit the points as closely as possible. In drawing the curves, the higher cumulative percentages have been emphasized because the lower results are believed to reflect the inherent weaknesses in some individual yarns. Furthermore, these yarns are probably not representative of the yarns as a whole.

The assumption that it is possible to use the same equation to obtain correction factors for different yarns is debatable. It is pointed out by Walker and Olmstead [3] that the ratio of multiple strands of yarns may vary with the kind of fiber. In this respect, it is interesting to note that, in Table VII, Kuralon 40/1 (1-ply, 131 den.) has an average of 42 observed cycles, whereas Kuralon 80/2 (2-ply, 130 den.) has an average of 210 observed abrasion cycles. Here we have an example of two yarns with the same kind of fiber, having the same denier, but the abrasion-resistance of the 2-ply yarn is roughly

TABLE VII. ABRASION RESISTANCE OF STAPLE YARNS

Identification*	Yarn fineness (den.)	Average cycles on modified Walker Abrader (n = 48) Actual results	Results adjusted to 100 den.†
Acetate 20/1	266	29	3
Orlon 16/1, Champlain	332	63	3
Decrystallized cotton 20/1	315	64	4
Nylon 30/2, Durham	365	93	4
Untreated cotton 20/1	267	59	5
Viscose 20/1	266	73	6
Wool 45/2 (metric)	410	467	13
Orlon 15/1, Newnan	352	424	18
Kuralon 40/1	131	42	21
Dacron 20/1, Dixie	266	255	21
Wool 28.4/1 (worsted)	284	388	28
Cotton 50/1	106	37	32
Fibravyl 75/1 (metric)	124	115	66
Nylon 60/1, Aberfoyle	88	73	100
Kuralon 80/2	130	210	108
Dacron 29/2, Nathan Schwartz	536	17,288	249
Dacron 60/2 (worsted), Phaar	278	9,192	696

* Numbering system is "cotton" unless otherwise indicated.
† These results were corrected to 100 den. using the factors obtained from Table V.

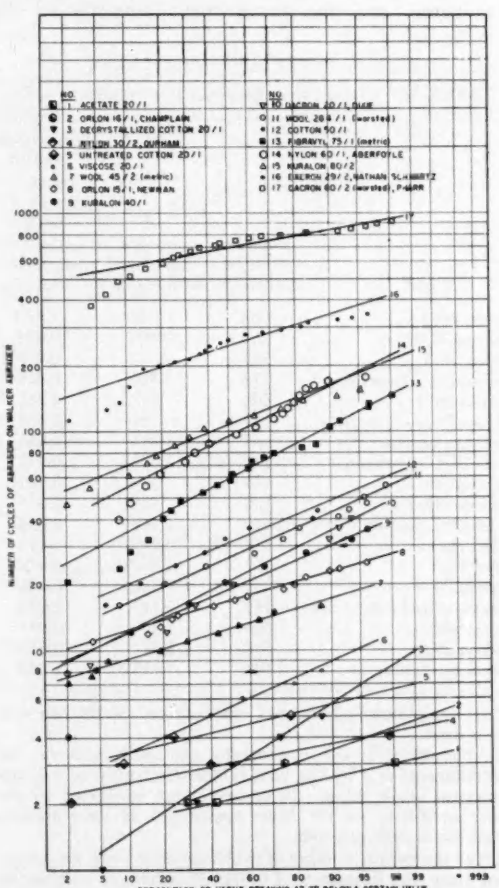

FIG. 7. *Abrasion resistance of staple yarns, corrected to 100 den.*

five times as great as for the 1-ply yarn. Thus it is seen that the effect of the number of plies and, perhaps, the twist are definite factors in the resistance to abrasion of yarns as measured by the Walker Abrader.

In comparing our results with those of Dr. Susich, it may be stated that both sets of results are, very roughly, similar. The greatest similarities are in the extremes. The multifilament abrasion results in both cases show that acetate and casein yarns are the most easily abraded, and nylon and Dacron yarns are the most resistant to abrasion. Also, the results of both investigations are in agreement with regard to the superiority of the abrasion resistance of filament yarns over the staple yarns.

However, there are several exceptions to the similarity of results. The outstanding exception is the difference in abrasion resistance of the two staple nylon yarns, as measured on the Walker Abrader. Susich shows these two yarns to have similar "relative abrasive damage." In Table VII it can be seen that these two yarns show widely differing resistances to abrasion when tested on the Walker Abrader. After this difference had been discussed with Dr. Susich, a second set of tests was run and the results were similar, within experimental error. It should be pointed out that the less resistant of the yarns, 30/2 Durham, is a 2-ply yarn, whereas the 60/1 is a singles yarn.

Examination of Dr. Susich's report [2] (Figure 8) shows that, when he used a high yarn tension (4.5 lbs.) in his tests, the cycle numbers at break of the same two yarns tended to be similar. However, as the tension was reduced, first to 1.5 lbs., and then to 0.5 lb., the differences between the number of cycles to produce a break increased. At a tension of 0.5 lb., the cycles to break of the Aberfoyle 60/1 nylon yarn was over three times greater than that of the Durham 30/2 nylon yarns. In our results it should be remembered that the tension on the yarns is very low. Thus at low tension our results more nearly approach those of Susich. Furthermore, it should not be overlooked that Susich's abrasive damage results of the two nylon yarns in question, which were based on observations at 120 abrasion cycles, and on which the relative ranking was based, were obtained at the high tension of 4 lbs. Susich [2] stated ". . . any change in the comparison level and in the severity of the tests would affect the abrasion results, and in some cases it might even affect the relative ranking of fibers with similar resistance to abrasion."

TABLE VIII. ABRASION DAMAGE OF VARIOUS TEXTILE FIBERS MEASURED ON THE MODIFIED WALKER ABRADER

Identification*	Type yarn	Yarn fineness (den.)	Average cycles adjusted to 100 den.†
Acetate 20/1	staple	266	3
Orlon 16/1, Champlain	staple	332	3
Decrystallized cotton 20/1	staple	315	4
Nylon 30/2, Durham	staple	365	4
Untreated cotton 20/1	staple	267	5
Viscose 20/1	staple	266	6
Wool 45/2 (metric)	staple	410	13
Orlon 15/1, Newnan	staple	352	18
Kuralon 40/1	staple	131	21
Dacron 20/1, Dixie	staple	266	21
Wool 28.4/1 (worsted)	staple	284	28
Cotton 50/1	staple	106	32
Acetate 100/40/2.5	multifilament	100	37
Casein 300/40	multifilament	300	54
Fibravyl 75/1 (metric)	staple	124	66
Nylon 60/1, Aberfoyle	staple	88	100
Kuralon 80/2	staple	130	108
Saran 200/12/5	multifilament	200	120
Dacron 29/2, Nathan Schwartz	staple	536	249
Orlon 100/40	multifilament	100	310
H.T. Fortisan 90/120/3	multifilament	90	322
Regular viscose 100/40	multifilament	100	385
Dacron 60/2 (worsted), Phaar	staple	278	696
Silk S 1303 (100 den.)	multifilament	100	720
Dacron 100/40	multifilament	100	3,919
Nylon Type 300, 100/40/2.5	multifilament	100	11,970

* Unless otherwise indicated, the "cotton" numbering system is used for the staple yarns.

† These results were corrected to 100 den. using the factors obtained from Tables III and V.

Conclusion

It should be emphasized that the yarn abrasive test on the Stoll-Quartermaster Abrader differs in yet another important detail from the Walker Abrader. On the Stoll machine, as each member of a bundle of yarns breaks, increasing tension is placed on the remaining yarns until a point is reached where the final rupture of yarns is due to excessive tension rather than prolonged abrasive action. In the case of the Walker Abrader, each yarn receives equal tension throughout the test, and only inherent differences in the yarns themselves result in breaks sooner or later in the duration of the test.

It has been demonstrated that the Walker Abrader has definite merit as a device for ranking yarns as to their resistance to abrasion.

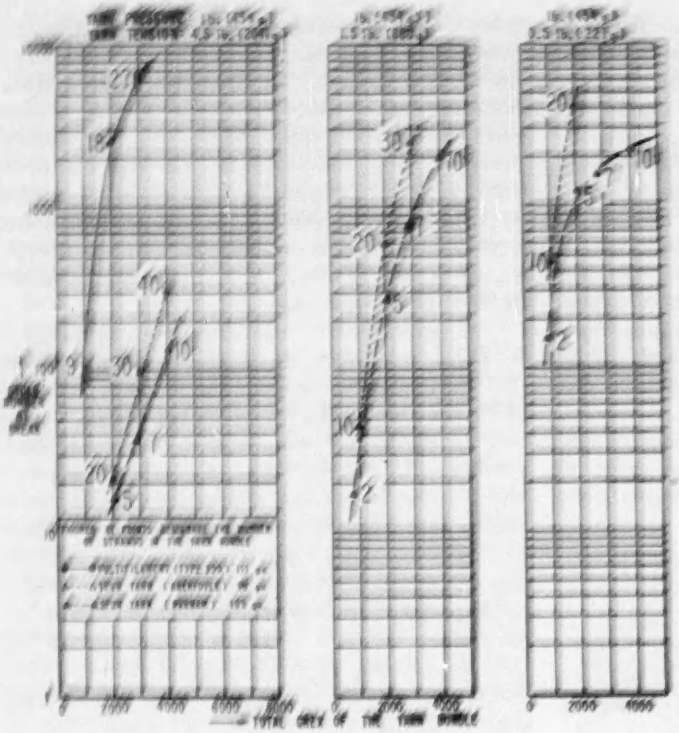

FIG. 8. Influence of bundle size (grex) of nylon yarns on cycle numbers. (Reproduced from Figure 11 of [2].)

Appendix

Derivation of the Equation $y = 174e^{0.0056x}$

(y = cycles on Walker Abrader; x = denier)

The four average abrasion-resistance values for viscose filament yarn 100/40, tested in multiples of one, two, three, and four strands, were plotted on semilogarithmic paper. An approximately straight line resulted. Therefore, the data may be fitted to an equation of the form [1]:

$$y = be^{cx}, \tag{1}$$

Taking the common logarithms of both sides of the equation:

$$\log y = \log b + (c \log e)x. \tag{1a}$$

Then, let $X = x$, $Y = \log y$, $B = \log b$, and $m = c \log e$ (slope of curve). Substituting in equation (1a) above, the equation for a straight line is obtained:

$$Y = mX + B.$$

Then solving the normal equations to determine B and m:

$$Bn + m\Sigma X = \Sigma Y, \tag{2}$$

$$B\Sigma X + m\Sigma X^2 = \Sigma XY. \tag{3}$$

x (den.)	y (Walker Abrader cycles avg.)
100	385
200	1151
300	2631
400	6153

	$X = x$	$Y = \log y$	X^2	XY
	100	2.5855	10,000	258.55
	200	3.0607	40,000	612.14
	300	3.4200	90,000	1026.00
	400	3.7506	160,000	1500.24
Totals	1000	12.8168	300,000	3396.93

Then equations (2) and (3) become:

$$4B + 1000m = 12.8168, \tag{4}$$

$$1000B + 300{,}000m = 3396.93. \tag{5}$$

Solving for B and m in equations (4) and (5):

$$B = \log b = 2.2406,$$
$$b = 174;$$

and

$$m = c \log e = 0.0039544,$$
$$c = 0.009.$$

Therefore, equation (1) becomes:

$$y = 174e^{0.009x}.$$

Derivation of the Equation $y = 0.001x^{2.53}$

(y = cycles on Walker Abrader; x = denier)

The four average values for Kuralon 80/2 staple yarn, tested in multiples of one, two, three, and four strands, were plotted on logarithmic paper. An approximately straight line resulted. Therefore, the data may be fitted to an equation of the form:

$$y = bx^m. \tag{1}$$

Taking the common logarithms of both sides of the equation:

$$\log y = m \log x + \log b. \tag{1a}$$

Then, let $Y = \log y$, $X = \log x$, and $B = \log b$. Substituting in equation (1a) above, the equation for a straight line is obtained:

$$Y = mX + B.$$

Then solving the normal equations to determine B and m:

$$Bn + m\Sigma X = \Sigma Y, \tag{2}$$

$$B\Sigma X + m\Sigma X^2 = \Sigma XY. \tag{3}$$

x (den.)	y (Walker Abrader cycles, avg.)
130	210
260	1630
390	3404
520	7282

	$X = \log x$	$Y = \log y$	X^2	XY
	2.1139	2.3222	4.468573	4.9088958
	2.4150	3.2122	5.832225	7.7574630
	2.5911	3.5320	6.713799	9.1517652
	2.7160	3.8622	7.376656	10.4897352
Totals	9.8360	12.9286	24.391253	32.3078592

Then equations (2) and (3) above become:

$$4B + 9.836m = 12.9286, \tag{4}$$

$$9.836B + 24.391253m = 32.3078592. \tag{5}$$

Solving for B and m in equations (4) and (5), we have:

$$m = 2.5256,$$
$$B = \log b = -2.9783,$$
$$b = 0.001051.$$

Therefore, equation (1) becomes:

$$y = 0.001x^{2.53}.$$

Acknowledgment

The authors wish to thank Dr. George Susich of the Quartermaster Research and Development Laboratories for supplying the yarns used in these experiments and for assistance in interpreting the results.

Literature Cited

1. Rider, P. R., "Analytic Geometry," New York, The Macmillan Co., 1947, pp. 268–77.
2. Susich, G., Abrasion Damage of Textile Fibers, TEXTILE RESEARCH JOURNAL **24**, 210–28 (Mar. 1954).
3. Walker, A. C., and Olmstead, P. S., Textile Yarn Abrasion Test, TEXTILE RESEARCH JOURNAL **15**, 201–22 (June 1945).

(Manuscript received September 1, 1954.)

Quantitative Spectrographic Analyses of Metallic Elements in Textile Materials

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Introduction

The mineral constituents of raw materials and finished products in the textile industry are frequently of much significance in relation to the quality of finishing and dyeing. Traces of the salts of aluminum, copper, or iron in the dye baths are frequent offenders which cause undesirable changes in shade. The presence of metallic elements in water used for finishing often causes subtle differences in the finish of the fabric.

These situations are merely examples of the effects of traces of metallic elements in textile products. Before these constituents can be eliminated, they must first be located both qualitatively and quantitatively. Wet chemical methods have offered a means of detection, but the techniques are often indirect and tedious, and small concentrations are at times never detected.

A rapid and precise means of analysis is offered by the spectrograph. The technique is the same for all metallic elements, the results are precise and accurate to as low a concentration as 1 part in 10 million, and a permanent record is obtained. Spectrographic analyses of both qualitative and quantitative natures have been carried on for some time in mineralogical work, steel manufacture, and oil refining. However, there has been very little application of this technique in the textile industry. This paper results from investigations carried on at Lowell Technological Institute in an effort to derive specific techniques on the preparation of textile materials for analysis, and on the performance of various methods of quantitative determination of metallic elements in textiles by spectrographic methods.

The fundamental theoretical premise for qualitative spectrographic analysis is the fact that, when an element is burned so that it is in an excited, vaporized state, characteristic electromagnetic radiation is emitted. This radiation is detected by means of a sensitized photographic plate mounted in the spectrograph on which the characteristic spectral lines are recorded. By means of suitable measuring instruments, tables, and charts, these wave-length lines and their associated elements are identified.

Spectrographic quantitative analysis is based on the premise that the intensity of a specific spectral line on the photographic plate is a function of the concentration of the element in the burned sample. By the control of operating conditions and the use of proper measuring instruments, readings of the line intensities and their associated element concentrations are determined.

Apparatus

The basic equipment that was used in the preparation of sample and the compilation of data for this paper is: Baird 3-meter grating spectrograph; JACO comparator microphotometer (nonrecording); Gaertner wave-length microcomparator; viewing box; agate mortar and pestle; Chain-o-matic balance; electrode cutter; Schaar electric muffle furnace; Shaker; photographic darkroom with standard equipment; source unit for direct-current arc; Bausch & Lomb spectrum-measuring magnifier.

Preparation of Sample

A bleached Osnaburg fabric was analyzed for this experiment. The fabric was cut into small strips, approximately 80 sq. in. in area, and each strip was weighed and placed in a Pyrex crucible. Ashing began to take place when the crucible containing the sample was heated in the open muffle furnace, which was set initially at 750°F. When all the fabric was carbonized, *i.e.*, when no more fumes came off, it was ignited strongly inside the muffle at a temperature of 1300°F until all the carbon was burned off. A good ashing was usually completed in 3 to 4 hrs., depending mainly on how closely the fabric was packed in the crucible.

In selecting chemical reagents for the analysis, care was taken to choose only those which contained very low concentrations of the contaminating elements for which the analyses were to be made.

The resultant ash (approximately 0.172% of the original weight) was mixed with pure graphite powder in a 1:1 ratio, and was ground in an agate mortar until a homogeneous mixture was obtained. A mechanical shaker may be used to achieve a better mixture. The graphite powder not only serves as a buffer mixture but also improves the conduction of the electric arc through the sample.

Qualitative Analysis

The mixture of fabric ash and graphite powder was packed into a ⅛-in.-deep crater drilled in the tip of a graphite electrode. With this electrode as positive pole and a counterelectrode of graphite as negative pole, a 5-amp. D.C. arc was struck to excite the specimen. The entire radiating area of the arc was focused on the grating of the spectrograph. The exposure was continued until all the sample appeared to have been volatilized. Under such conditions the more volatile elements were vaporized in the initial stages, and the more refractory elements fused down to a bead at the bottom of the crater and were vaporized more slowly. Complete vaporization of the mixture was necessary for a reliable analysis. A rotating-sector disc with a factor of ¼ was located in front of the slit at the secondary stigmatic focus to decrease the intensity of exposure; *i.e.*, for 80-sec. burning, the actual exposure time was reduced to 20 sec.

The plate for the qualitative analysis was taken in the 2700–3395-Å. region in the second order with exposure times of 5–18 secs.

The resultant plate was examined using a Gaertner microcomparator for wave-length identification. By referring to the M.I.T. wave-length tables, it was found that the fabric contained silicon, iron, aluminum, copper, and sodium (see Table I).

Since the presence of iron in textile materials has caused the most trouble in finishing and dyeing and since the iron is most likely to be picked up in all stages of manufacture, it was decided to limit this investigation to that constituent only. However, the methods devised are equally applicable to any of the metallic elements.

TABLE I. EVALUATION OF PLATE TAKEN FOR QUALITATIVE ANALYSIS

Line no.	Observed wave length (Å.)	Tabular wave length (Å.)	Element
1	2881.48	2881.58	Si
2	3020.64	3020.64	Fe
3	3082.13	3082.15	Al
4	3092.81	3092.71	Al
5	3247.54	3247.54	Cu
6	3273.96	3273.96	Cu
7	3302.40	3302.87	Na
8	3303.06	3302.99	Na

Quantitative Analysis

There are several techniques for spectrographic quantitative analysis, but they are basically variations in the methods of comparing the density of a line in the spectrum of the sample to the density of a line of a standard spectrum in which the concentration of the element present is known. The four methods used in the work described herein were: (*1*) the internal-standard method; (*2*) the modified internal-standard method; (*3*) the logarithmic-sector method; and (*4*) the addition method.

A complete analysis was performed by each of these methods, and comparisons were then made of the relative advantages and limitations of each method.

Internal-Standard Method

Gerlach introduced his principle of "internal standard" in the middle of the 1920's. He chose a reference pair consisting of a line of the analysis element and a line of the reference or standard element which has approximately the same intensity at that concentration. It is then assumed that, if the two lines of a reference pair appear with equal intensity in the spectrum of any sample, the concentration of the analysis element will be the same as in the reference samples whose spectra had been previously studied. This basic assumption of the internal-standard method can be expressed by the simple relationship

$$\log \frac{I_a}{I_s} = \log \frac{K_a}{K_s} + \frac{n_a}{n_s} \log \frac{C_a}{C_s},$$

where I_a and I_s are the relative intensities of the analysis line and reference line, respectively; K_a and K_s are their respective constants; n_a and n_s are their respective emission factors; and C_a and C_s are the respective concentrations of analysis and reference elements. Since, by definition, C_s should always be present in constant amount, this equation can be written as

$$\log \frac{I_a}{I_s} = \log K + n_a \log C_a.$$

Analysis of an unknown sample can be carried out

by selecting visually the one of these reference pairs in the spectrum for which the two lines are of equal intensity. Most of the modern procedures use only one such pair of lines. Their relative intensities are determined by the microphotometer. If the two variables (I_a/I_s vs. C) are plotted in logarithmic scales, the resulting analytical curve over a considerable range is usually very close to a straight line of 45° slope. After preparing such a calibration graph for each analysis element, any sample of comparable composition can easily be analyzed by measuring line-intensity ratios and reading concentration from the graphs.

The advantage of using an internal standard is that any variations in the reference line would provide automatic correction for variations in excitation, optical alignment, exposure, and, to a limited extent, for variations in the response of the photographic emulsion. Most of these variables other than concentration should affect the measured intensities of the analysis line and reference line to the same degree. Unfortunately, the last statement is true only where the ionization and excitation potentials of the two elements are similar. Hence, it is essential to select a pair of lines which behave as similarly as possible under varying conditions; such line pairs were called by Gerlach "homologous pairs." Since proximity on the plate minimizes errors due to variation in emulsion sensitivity from point to point, and proximity in wave length avoids variation in plate contrast, a line pair may be selected by choosing a reference element of approximately the same ionization potential, the same rate of volatilization, and roughly the same wave length as the analysis element. Once chosen, the concentration of the reference element or internal standard should be so adjusted that its line intensity lies at a level which is approximately at the middle of the range of intensities of the analysis line used.

Two types of internal-standard lines may be used: (*1*) a weak line of the element which is the major constituent of the sample and is known to be constant in intensity within the limits of experimental observation; and (*2*) a strong or persistent line in the spectra of an added small amount of an element which is known not to be present in either the known or the unknown sample. In the present study, cobalt was selected as the internal standard, because it was not present in the sample and the wave lengths of several of its persistent lines were in the wavelength range being used, 2700–3395 Å. in the second-order region. Its ionization potential of 8.5 v. is similar to that of iron, which is 7.8 v. Furthermore, many of the cobalt lines have excitation potentials similar to the iron lines under study.

In determining the amount of iron present in the fabric, the authors used the cobaltous nitrate (20.25% Co) and ferric ammonium sulfate (11.58% Fe) for the preparation of standards. The compounds of the elements sought were weighed, and the ratios of their weights to that of the base mixture were adjusted to give an initial standard which contained 2.0%, 1.5%, 1.0%, 0.5%, 0.1%, and 0.03% iron. Mixing was carried out in an agate mortar and mechanical shaker.

Preparation of Samples with 2% Cobalt Standard

Material in mixture	Weight (mg.)	Composition (%)
Fabric ash	200.0	50
Cobaltous nitrate	39.5*	2
Pure carbon	160.5	—
Total wt. of sample	400.0	

Preparation of Standards (Including 2% Cobalt)

Material in mixture	Weight (mg.)	Composition (%)
Ferric ammonium sulfate	345.3†	2
Cobaltous nitrate	197.5	2
Pure carbon	1457.2	—
Total wt. of standard	2000.0	
Ferric ammonium sulfate	258.9	1.5
Cobaltous nitrate	197.5	2
Pure carbon	1543.6	—
Total wt. of standard	2000.0	
Ferric ammonium sulfate	172.7	1.0
Cobaltous nitrate	197.5	2
Pure carbon	1629.8	—
Total wt. of standard	2000.0	
Ferric ammonium sulfate	86.3	0.5
Cobaltous nitrate	197.5	2
Pure carbon	1716.2	—
Total wt. of standard	2000.0	
Ferric ammonium sulfate	17.3	0.1
Cobaltous nitrate	197.5	2
Pure carbon	1785.2	—
Total wt. of standard	2000.0	
Ferric ammonium sulfate	5.2	0.03
Cobaltous nitrate	197.5	2
Pure carbon	1797.3	—
Total wt. of standard	2000.0	

* 39.5 mg. of cobaltous nitrate contains only 39.5 × 20.25% = 8.0 mg. of cobalt. This amounts to 2% of the total weight of the sample.

† 345.3 mg. of ferric ammonium sulfate contains only 345.3 × 11.58% = 40 mg. of iron. This amounts to 2% of the total weight of the standard.

These standards were then burned in a manner that duplicated as closely as possible the burning of the unknown sample.

Electrode shapes and sizes similar to those in qualitative analysis were used; however, for quantitative analyses involving very low concentrations, it is important to arc a smaller weight of sample in the electrode in order to dissociate all molecules present into their constituent atoms and to cause every atom of the element of interest to emit as much radiation as possible. The following conditions were maintained for the preparation of working curves and quantitative determination of iron by the internal-standard and modified internal-standard methods.

Exposure Conditions

Plate type	Eastman Kodak II-0
Spectral region	5400–6790 Å.
Slit width	75 μ
Slit length	2.5 mm.
Exposure time	20 sec.
D.C. current	5 amp.
Arc-gap width	6 mm.
Sector disc	1/4 factor

Photographic Processing

Developing	Eastman D-19	2 min. at 73°F
Stop bath	Acetic acid	½ min.
Fixing	Acid fixer	8 min.
Washing	Running water	20 min.

The resulting plate was examined using a Gaertner microcomparator for locating the cobalt lines and a JACO microphotometer for measuring the line intensity. For the internal-standard method, the authors chose Fe: 3020.6 and Co: 3044.0 as the reference pair because these two lines have about equal intensities (to simplify the comparison of intensity) and are close together (to simplify photometric problems). Furthermore, they produce a straight-line working curve having a slope of 45° in the concentration range which is of interest.

Since the internal-standard method involves the determination of intensity ratios, the first step in the procedure is the conversion of the data obtained from the microphotometer to relative intensities. This can be accomplished by referring to the characteristic curve, sometimes known as the "calibration curve," in which the density of the photographic image is plotted against the relative intensity of the light producing the image. In usual analytical work, so long as the emulsion, the developing process, and other factors are controlled, it is sufficient to establish only one calibration curve for the spectral range used.

Of the many possible methods for obtaining an intensity (or time-of-exposure) variation, a logarithmic sector disc was used in connection with this work. The disc was cut in such a way that, when it was rotated rapidly in front of the spectrograph slit, a series of exposures was allowed to reach the plate with a gradual density change in the lines. The height of these lines from a given base would be a logarithmic function of the intensity of the lines in the source, while the density was obtained from the logarithm of the galvanometer deflection ratio (d_0/d). The resultant graph, drawn by plotting d_0/d vs. intensity on semilog coordinates, shows a characteristic curve like that in Figure 1.

The measurements for this characteristic curve were taken near the 3034-Å. region. The line used for the calibration was divided into thirteen segments in which the height was measured by the microcomparator, and the galvanometer deflection by the microphotometer. The results of the measurements are shown in Table II.

TABLE II. DATA FOR THE CHARACTERISTIC CURVE

No.	Height (mm.)	Average	Relative intensity	d	d_0/d*
0	——				
1	1.058	0.529	188.9	4.6	21.1
2	2.108	1.583	63.2	5.6	17.3
3	3.177	2.642	37.8	7.6	12.8
4	4.014	3.595	27.8	9.5	10.2
5	5.247	4.630	21.6	13.5	7.2
6	6.299	5.773	17.3	19.2	5.1
7	7.487	6.893	14.5	26.6	3.7
8	8.196	7.841	12.7	40.0	2.4
9	9.490	8.843	11.3	52.6	1.8
10	10.483	9.987	10.0	66.5	1.5
11	11.653	11.068	9.0	85.4	1.2
12	12.691	12.171	8.2	87.6	1.1
13	13.885	13.288	7.6	92.2	1.0

* $d_0 = 97.0$ = deflection for the clear portion on the photographic plate.

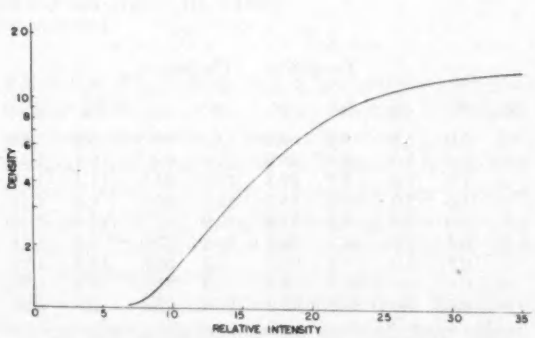

FIG. 1. *Characteristic curve used for plate calibration and background correction.*

In most spectrographic procedures, the excitation conditions, the optical arrangement, and the exposure time are usually selected with a view towards keeping spectral background to a minimum. This background is due mainly to the emission of continuous radiation from the electrode tips, incandescent particles within the source column, and scattered radiation within the spectrograph. When determining small amounts of certain constituents by either arc or spark techniques, excessive spectral background is sometimes unavoidable. In such cases the analyst has no recourse but to make a correction for background, since the reduction in the sensitivity of the test by inclusion of background in the measurements would increase the random error of analysis. However, the amount of background which may be tolerated without correction depends upon the absolute reproducibility of densities, the source of the background, the degree to which the photographic emulsion shows the Eberhart effect, and the accuracy required of the analysis. The proper correction is to determine the background intensity and line intensity from the calibration curve and subtract the former from the latter to obtain the true line intensity. It should be noted that background correction involves a difference in intensity (I) rather than log I, and for this reason it may be convenient to prepare a density-intensity curve for calibration purposes.

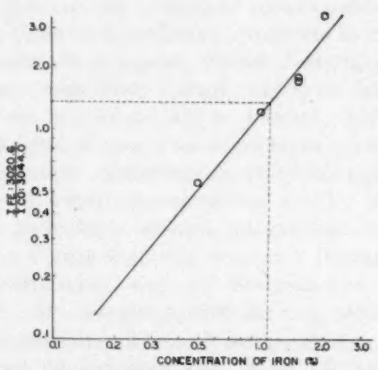

FIG. 2. *Working curve for the internal-standard method. Fe:3020.6; Co:3044.0.*

Under the assumption of the internal-standard method, the intensity ratio (I_a/I_s) for a particular material is a function of the single variable, concentration. Therefore, when the value of I_a/I_s has been determined, as described above, concentration can be determined if sufficient data on samples of known composition are available. The correlation of such data (see Table III) is generally accomplished graphically, and, because of the nature of the mathematical relationship between concentration and the intensity function, it is convenient to use log-log coordinates. Such a graph is called a "working curve." For the purpose of this discussion, the working curve is defined as a graph on which concentration (%) is plotted logarithmically on the abscissa scale against I_a/I_s plotted logarithmically on the ordinate scale.

In many cases the working curve is a straight line within the ranges of concentration covered by a particular line pair. In most routine work the assumption of linearity is sufficiently valid. Self-reversal, failure to correct for excessive background at the analysis line, and the effects of increasing concentration on the behavior of the internal-standard line each may contribute to curvature of the working curve.

TABLE III. DATA FOR THE PREPARATION OF THE WORKING CURVE (INTERNAL-STANDARD METHOD)

No.	% Fe	% Co	Fe:3020.6 d	Fe:3020.6 d'	Co:3044.0 d	Co:3044.0 d'	$\frac{d_0}{d_{Fe}}$*	$\frac{d_0}{d'_{Fe}}$*	$\frac{d_0}{d_{Co}}$*	$\frac{d_0}{d'_{Co}}$*	Fe I	Fe I'	I_{Fe}	Co I	Co I'	I_{Co}	$\frac{I_{Fe}}{I_{Co}}$
1	2.0	2.0	7.2	69.7	15.2	66.3	13.6	1.41	6.4	1.48	42.3	9.9	32.4	19.3	10.2	9.1	3.56
2	1.5	2.0	10.8	86.9	21.6	89.8	9.1	1.13	4.6	1.09	23.0	8.5	14.5	16.6	8.2	8.4	1.73
3	1.5	2.0	8.7	82.5	15.2	87.7	11.3	1.19	6.4	1.12	28.3	8.9	19.4	19.3	8.4	10.9	1.78
4	1.0	2.0	10.7	86.0	15.7	93.1	9.2	1.14	6.2	1.05	23.1	8.6	14.5	19.0	7.7	11.3	1.28
5	1.0	2.0	7.2	83.8	9.0	97.1	13.6	1.17	11.9	1.01	42.3	8.7	33.6	34.0	7.0	27.0	1.25
6	0.5	2.0	48.7	80.8	50.6	97.0	2.0	1.21	1.9	1.01	11.6	9.0	2.6	11.5	7.0	4.5	0.58
7	0,5	2.0	7.1	89.1	5.3	88.4	13.8	1.10	18.5	1.11	43.5	8.2	35.3	69.2	8.2	61.0	0.58
8	0.1	2.0	26.1	79.8	4.0	81.7	3.8	1.23	24.5	1.20	15.3	9.1	6.2	90.5	8.9	81.6	0.076
9	0.03	2.0	87.8	92.6	17.6	92.2	1.1	1.06	5.6	1.06	8.4	7.7	0.7	18.1	7.7	10.4	0.067

* $d_0 = 98.0$.

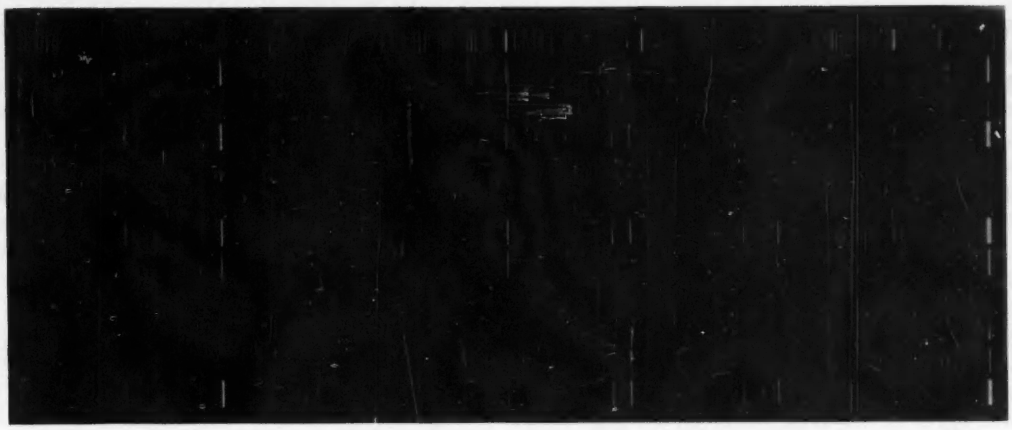

FIG. 3. *Spectrogram for quantitative analyses.*

TABLE IV. ANALYSIS OF IRON IN FABRIC ASH
(INTERNAL-STANDARD METHOD)

	Fe:3020.6		Co:3044.0						Fe			Co				
No.	d	d'	d	d'	$\frac{d_0}{d_{Fe}}$*	$\frac{d_0}{d'_{Fe}}$*	$\frac{d_0}{d_{Co}}$*	$\frac{d_0}{d'_{Co}}$*	I	I'	I_{Fe}	I	I'	I_{Co}	$\frac{I_{Fe}}{I_{Co}}$	% Fe
1	18.5	46.3	24.3	49.2	3.9	1.56	3.0	1.46	15.5	10.4	5.1	13.8	10.1	3.7	1.38	1.08
2	3.8	8.2	4.1	7.2	18.9	8.78	17.6	9.99	100.0	22.5	77.5	73.5	24.7	58.8	1.32	1.06
3	7.7	44.3	11.0	39.8	9.3	1.63	6.6	1.81	23.5	10.6	12.9	19.4	11.1	8.3	1.55	1.21
4	7.2	34.0	10.0	30.7	10.0	2.12	7.2	2.35	24.8	11.9	12.9	20.3	12.5	7.8	1.65	1.26
5	19.5	57.9	24.0	59.1	3.7	1.24	3.0	1.22	15.2	9.2	6.0	13.9	9.1	4.8	1.25	1.01
6	14.3	53.0	17.0	45.6	5.1	1.36	4.2	1.58	17.3	9.7	7.6	16.1	10.5	5.6	1.36	1.07
7	36.8	70.5	41.0	65.2	2.0	1.02	1.8	1.11	11.5	7.3	4.2	11.0	8.3	2.7	1.55	1.21
8	10.7	35.0	12.3	29.9	6.7	2.06	5.9	2.41	19.7	11.8	7.9	18.5	12.7	5.8	1.36	1.07
9	11.6	71.5	14.8	66.4	6.2	1.01	4.9	1.09	19.0	7.0	12.0	17.1	8.1	9.0	1.33	1.06

* $d_0 = 72.0$.

Once the working curve is plotted (see Figure 2) it can be used directly for the determination of percent constituent if I_a/I_s is known.

After the working curve was established, a plate was made under the standard conditions to carry out the quantitative analysis of the iron content in the fabric ash. Figure 3 shows a photograph of this spectrogram. Table IV shows the results of the nine analyses of the same fabric ash. The iron concentrations were evaluated by using the working curve of Figure 2.

In order to evaluate the statistical reproducibility of this method, the mean value and deviations from the mean were determined. The mean value for the iron concentration in the fabric ash was 1.11%, with an average deviation from the mean of ±0.07. This represented a deviation of ±6.6% (see Table V).

Modified Internal-Standard Method

When restricting all photometric measurements to the approximately straight-line portion of the characteristic curve and assuming that

$$\log \frac{I_a}{I_s} = K \log \frac{d_a}{d_s},$$

where I is the intensity and d the galvanometer deflection (with subscripts a and s referring to analysis and internal-standard lines, respectively), the deflection ratios d_a/d_s may be used directly in place of intensity ratios I_a/I_s. By plotting log concentration *vs.* log (d_a/d_s), a different working curve can be obtained. This deflection ratio method is here called the "modified internal-standard method."

The procedure involved differs from the more general one of converting the galvanometer deflec-

tions to relative intensities by the use of a calibration curve and plotting the calculated intensity ratios against concentration. The technique employed in this modified internal-standard method has been found to save time, since preparation of a characteristic curve and conversion of galvanometer deflections to relative intensities are obviated. However, this saving is at the expense of some precision because an accurate correction cannot be made for the background.

The same plates that were originally used to prepare the working curve and determine the iron content by the original method were also utilized for this modified internal-standard method. Table VI shows the data used for the preparation of the modified internal-standard working curve (see Figure 4).

TABLE V. STATISTICAL PRESENTATION OF THE REPRODUCIBILITY FOR THE INTERNAL-STANDARD METHOD

Analysis No.	% Fe	Deviation from mean
1	1.08	0.03
2	1.06	0.05
3	1.21	0.10
4	1.26	0.15
5	1.01	0.10
6	1.07	0.04
7	1.21	0.10
8	1.07	0.04
9	1.06	0.05
Total	10.03	0.66
Mean	1.11	0.07

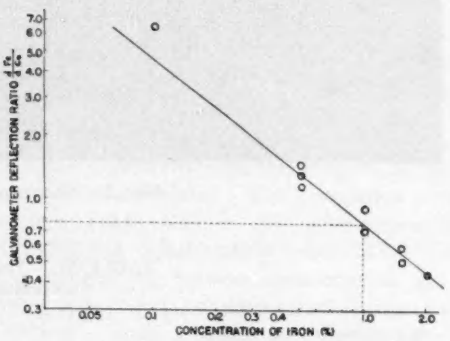

FIG. 4. *Working curve for the modified internal-standard method. Fe: 3020.6; Co: 3044.0.*

TABLE VI. DATA FOR THE PREPARATION OF THE WORKING CURVE (MODIFIED INTERNAL-STANDARD METHOD)

No.	% Fe	% Co	Fe:3020.6 d	Fe:3020.6 d'	Co:3044.0 d	Co:3044.0 d'	d_0	Corrected d* Fe	Corrected d* Co	$\frac{d_{Fe}}{d_{Co}}$
1	2.0	2.0	7.2	69.7	15.2	66.3	98.0	10.3	22.9	0.45
2	1.5	2.0	10.8	86.9	21.6	89.8	98.0	12.4	24.1	0.52
3	1.5	2.0	8.7	82.5	15.2	87.7	98.0	10.6	17.3	0.61
4	1.0	2.0	10.7	86.0	15.7	93.1	98.0	12.4	16.9	0.74
5	1.0	2.0	7.2	83.8	9.0	97.1	98.0	8.6	9.3	0.93
6	0.5	2.0	48.7	80.8	50.6	97.0	98.0	60.3	52.2	1.16
7	0.5	2.0	7.1	89.1	5.3	88.4	98.0	8.0	6.0	1.33
8	0.5	2.0	9.2	88.2	6.4	91.5	98.0	10.4	7.0	1.49
9	0.1	2.0	26.1	79.8	4.0	81.7	98.0	32.7	4.9	6.68

* d is corrected by $(d_0/d') \times d$.

TABLE VII. ANALYSIS OF IRON IN FABRIC ASH (MODIFIED INTERNAL-STANDARD METHOD)

No.	Fe:3020.6 d	Fe:3020.6 d'	Co:3044.0 d	Co:3044.0 d'	d_0	Corrected d Fe	Corrected d Co	$\frac{d_{Fe}}{d_{Co}}$	% Fe
1	18.5	46.3	24.3	49.2	72.0	40.0	49.4	0.810	0.94
2	3.8	8.2	4.1	7.2	72.0	46.4	56.9	0.816	0.93
3	19.5	57.9	24.0	59.1	72.0	34.7	40.7	0.853	0.88
4	14.3	53.0	17.0	45.6	72.0	27.0	37.3	0.724	1.07
5	36.8	70.5	41.0	65.2	72.0	52.3	62.9	0.832	0.91
6	10.7	35.0	12.3	29.9	72.0	30.6	41.2	0.743	1.04
7	11.6	71.5	14.8	66.4	72.0	16.2	22.3	0.727	1.06

Table VII shows the results of the analyses for iron content by this method. Only seven analyses were determined in this case because the values of two of them were beyond the range of the working curve.

A statistical evaluation of the reproducibility of this method showed the mean value of the iron concentration in the ash to be 0.98%, with a deviation from the mean of ±0.07. This represented a deviation of ±7.1% (see Table VIII).

Logarithmic-Sector Method

The use of logarithmic-sector discs as a means of measuring intensities in quantitative analysis was first introduced by Scheibe and Neuhausser in 1928. They used a rotating disc with its periphery cut to the shape of a logarithmic spiral (see Figure 5a) whose equation was

$$-\log \theta = C + kL,$$

where θ = angle of the sector arc, C and k = constants, and L = radial distance from the sector periphery to the circumscribing circle. This sector disc, when placed at the focal point of the grating, would reduce the intensity of the light passing through the slit and attenuate the degree of blackening of a photographed line, thus giving the appearance shown in Figure 5b. In this way, the height of a line becomes a measure of the logarithm of its intensity. Assuming that the photographic plate is capable of integrating intermittent exposures so as to compare exposures of shorter time and greater intensity with longer time and weaker intensity, an equal blackening of the photographic plate will be produced at points along the graded spectrum line where the light intensity is the same. In other words, the intensity of two lines at the pointed end will be the same. Since the height of each of the two lines is proportional to the logarithm of its intensity, the difference in their heights is a direct measure of the difference in the logarithms of their intensity values and is equal to the logarithm of the intensity ratio of the two lines.

In applying this logarithmic-sector method to quantitative analysis, several standard mixtures must first be prepared. These must contain constant known percentages of the internal standard and varying known percentages of the metal to be determined. The internal standard should be selected on the basis of the homologous-pair principle. For convenience sake, the authors used the same mixtures which were prepared for the internal-standard method. After the spectra of these standards and samples had been photographed, the heights of homologous lines were measured with a spectrum-measuring magnifier whose scale is divided into tenths of a millimeter.

In the comparison of two lines such as an internal-standard and an analysis line, the height of each line is a measure of its intensity and the logarithm of

TABLE VIII. STATISTICAL PRESENTATION OF THE REPRODUCIBILITY FOR THE MODIFIED INTERNAL-STANDARD METHOD

Analysis No.	% Fe	Deviation from mean
1	0.94	0.04
2	0.93	0.05
3	0.88	0.10
4	1.07	0.09
5	0.91	0.07
6	1.04	0.06
7	1.06	0.08
Total	6.83	0.49
Mean	0.98	0.07

FIG. 5. *Logarithmic-sector disc.* Top—*Disc.* Bottom —*Appearance of spectrum lines of different intensity.*

the ratio of the intensities is expressed as

$$L_a - L_s = a \log \frac{I_a}{I_s}.$$

This difference remains the same for various conditions of exposure, slit width, development, and plate characteristics, as long as the sector gradient is sufficient to include the transmission required to produce the same selected density in both lines. The algebraic difference between the heights of these two lines is then plotted as one of the variables in the working curve against the logarithm of the percent concentration (see Figure 6).

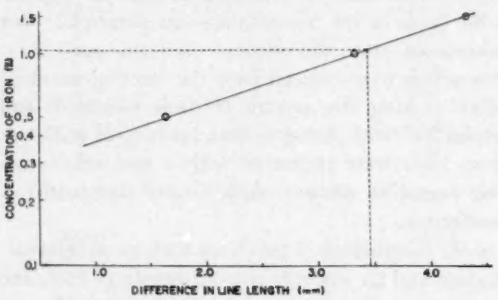

FIG. 6. *Working curve for the logarithmic-sector method. Fe:3020.6; Co:3017.5.*

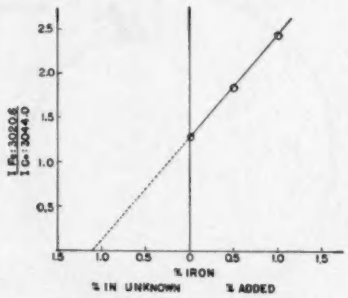

FIG. 7. *Working curve for the addition method. Fe:3020.6; Co:3044.0.*

A plate was made for the preparation of the working curves and for the quantitative determination of iron in the fabric ash by means of this logarithmic-sector method. The results of analysis evaluated from the curve of Figure 6 are shown in Table IX.

Addition Method

One of the simplest methods of preparing a standard is to take some of the actual material being analyzed as the base material and add to it known amounts of the elements to be determined. At least two standards should be prepared, in which the amount added may be made to vary by a factor of 2. For instance, if $x\%$ = concentration of the iron sought in the fabric ash and 0.5% and 1.0% iron are added, the standards will have $(x + 0.5)\%$ and $(x + 1.0)\%$ of iron. A plot is then made of percent iron added *vs.* intensity ratio of the analysis pair, using ordinary coordinates. The unknown or fabric ash is included in this plot and is equivalent to the plot of 0% of added material. If all the points fall on a straight line, an extrapolation may be made. The intercept of this extrapolation with the abscissa gives the concentration of iron sought in the fabric ash.

It is important to note that self-absorption must be absent when using this addition method. This

TABLE IX. ANALYSIS OF IRON IN FABRIC ASH (LOGARITHMIC-SECTOR METHOD)

Mixture	Concentration		Heights of lines (mm.)			
	% Fe	% Co	Fe:3020.6	Co:3017.5	Diff.	% Fe
1	0.5	2.0	9.2	7.6	1.6	
2	1.0	2.0	9.5	6.2	3.3	
3	1.5	2.0	8.4	4.1	4.3	
Ash*	?	2.0	6.3	2.9	3.4	1.04
Ash*	?	2.0	7.6	4.1	3.5	1.04

* From the working curve shown in Figure 6, the average iron content in the fabric ash was found to be 1.04%.

TABLE X. ANALYSIS OF IRON IN FABRIC ASH (ADDITION METHOD)

No.	% Co	% Addition of iron	Fe:3020.6 d	Co:3044.0 d	$\frac{d_0}{d_{Fe}}$*	$\frac{d_0}{d_{Co}}$*	I_{Fe}	I_{Co}	$\frac{I_{Fe}}{I_{Co}}$	% Fe
1	2.0	0	13.6	24.0	7.2	4.08	20.5	15.8	1.30	
2	2.0	0.5	9.8	36.2	10.0	2.71	24.7	13.3	1.85	
3	2.0	1.0	7.8	24.9	12.6	3.93	38.0	15.5	2.45	1.10

* $d_0 = 98.0$. No correction for background was necessary because of the exceptionally clear plate.

can easily be checked by plotting at least three points and observing whether or not there is linearity. Correction should also be made for the background if it is appreciable.

The accompanying data show the preparation of standards which were adjusted to give an initial addition of 0.0%, 0.5%, and 1.0% of iron. The resultant plate was analyzed using the JACO microphotometer, the result of which is shown in Table X. The working curve used is shown in Figure 7.

Preparation of Standards (Including 2% Cobalt)

0% Addition

Fabric ash	200.0 mg.
Cobaltous nitrate*	39.5
Pure carbon	160.5
Total wt. of standard	400.0 mg.

0.5% Addition

Fabric ash	150.0 mg.
Cobaltous nitrate	29.7
Ferric ammonium sulfate†	12.9
Pure carbon	107.4
Total wt. of standard	300.0 mg.

1.0% Addition

Fabric ash	150.0 mg.
Cobaltous nitrate	29.7
Ferric ammonium sulfate	25.9
Pure carbon	94.4
Total wt. of standard	300.0 mg.

* Concentration of cobalt in cobaltous nitrate = 20.251%.
† Concentration of iron in ferric ammonium sulfate = 11.585%.

TABLE XI. SUMMARY OF DATA

Methods of analysis	% Fe in fabric ash	% Fe with respect to fabric weight*
Internal standard	1.11	0.00382
Modified internal standard	0.98	0.00337
Logarithmic sector	1.05	0.00361
Addition	1.10	0.00378

* Average ash content with respect to fabric weight was found to be 0.172%. Since the ash was diluted with other constituents at a 1:1 ratio, all the experimental results can be corrected to percent iron with respect to fabric weight as follows: % Fe × 2 × 0.00172.

Conclusion

A summary of the results of the four methods of analysis is given in Table XI.

An evaluation of the techniques of quantitative spectrographic analyses reveals the following:

1. The amount of textile materials required in spectrographic analysis is extremely small; a few milligrams suffice in many cases for a complete qualitative and quantitative analysis for the metallic constituents. The nature or condition of the sample fabric is immaterial to the analysis techniques.

2. A minimum amount of chemical preparation and handling of the sample for analysis is required.

3. A statistical evaluation of the results obtained by the four methods shows that there is no significant difference among the methods.* Slight discrepancies in the homogenity of the samples may be the cause of the small variations in results. The internal-standard method is the most accurate, while the logarithmic-sector method is the simplest and quickest to perform.

4. Upon the completion of working curves and standard mixtures in the laboratory, quantitative analysis of samples for their metallic content can be accomplished very expeditiously. Using the logarithmic-sector method, as many as twenty analyses per hour may be completed. The other methods also present great time savings over wet chemical methods.

5. Spectrographic quantitative analyses determine concentrations of trace elements which would normally be undetected by conventional chemical methods.

Bibliography

1. Ahrens, L. H., "Spectrochemical Analysis," Cambridge, Mass., Addison-Wesley Press, 1950.
2. Brode, W. R., "Chemical Spectroscopy," 2nd ed., New York, John Wiley & Sons, Inc., 1945.
3. Harrison, G. R., Lord, R. C., and Loofbourow, J. R., "Practical Spectroscopy," New York, Prentice-Hall, Inc., 1948.
4. Sawyer, R. A., "Experimental Spectroscopy," New York, Prentice-Hall, Inc., 1944.

(Manuscript received August 9, 1954.)

* Statistical *T* tests were performed on the results of the four methods. In all four cases, the results showed no significant difference at the 5% level.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Micronaire-Fineness and Causticaire-Maturity Relationships

LABORATORIUM DE MEULEMEESTER
Gent, Belgium
April 4, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

With reference to the "Letter to the Editor" entitled "The Relationship Between Micronaire-Fineness and Causticaire-Maturity for Various Cotton Samples," by W. F. du Bois and D. F. van de Riet, in TEXTILE RESEARCH JOURNAL, page 265, March, 1954, we wish to make the following comments.

What is Measured by the Micronaire?

If due consideration is given to the physical property which is determined by permeability measurements, it will be possible to avoid many misconceptions.

The Micronaire is really a flowmeter and, as a first approximation, flow may be assumed to be in direct relation with the float level. It has been shown [1] that the extreme low and high float-level readings do not vary quite linearly with the float position. But, with these exceptions, a linear scale reading will furnish a flow measurement. The laws of flow through porous media have shown that the square of the specific surface of the fiber is in first approximation inversely proportional to the air flow. Consequently, the air flow read by the float level can be considered as a measure of the specific surface of the fiber [3].

It is reasonable to correlate specific surface with other terms more commonly employed, such as weight fineness, or maturity, or flattening. Nevertheless, it is unwise to represent the relation too simply. The "Micronaire index" is a measure neither of gravimetric fineness nor of the degree of maturity or flattening; it should be considered as indicating a combination of physical properties which influence the float level in one direction or the other.

What Scale Should Be Used?

From the above it follows that we can and may use the term Micronaire *fineness* so far as cotton varieties or types with approximately the same maturity degree and flattening are concerned, in which case the scale can be calibrated in units of weight fineness. The curvilinear scale commonly used represents a measure of weight fineness when American Upland cotton with its own maturity average, or any other similar cotton, is to be tested. This is one of the reasons why, on the one hand, more scales have been developed by the Cotton Branch, U. S. Department of Agriculture, for use in testing American Egyptian, etc. [5], and why, on the other hand, the correlation between weight fineness and Micronaire index (linear scale) calculated for cottons representing a large range including very low maturity gives no satisfaction [3].

In our opinion it is wise to adopt a linear scale and to recognize that the readings on the Micronaire are influenced by the weight fineness, maturity, and flattening degree. The return to a linear scale (with exception of extreme values) in connection with the Causticaire method is very logical.

The brief explanation above will serve to clarify our answers to the questions raised by the authors of the "letter."

(*1*) and (*2*) The Micronaire index is through maturity and degree of flattening influenced by the soil and climate as well as growth conditions of the cotton plant. The average perimeter, which is a

varietal property, as well as the fact that the fiber is more or less collapsed—in other words shows a lumen volume which may be greater or less in proportion to total fiber volume—indicates that the Micronaire index depends also on variety.

The practical limits 3.5 and 4.0 Micronaire indices (curvilinear scale) mentioned in the letter are significant for the commercial cotton types that were examined. Analogous limits determined in the same way on Congo cotton varieties in selection, which vary markedly in maturity are 3.5 and 4.8 on curvilinear scale.

(*3*) Maturity limit "76%" has in our opinion no practical significance and is given by the U. S. Department of Agriculture laboratories in the form of an easy-to-use table which helps to compare quickly, but approximately, different cottons in connection with maturity. In spinning and dyeing problems it is of major importance to make no blendings of cottons which differ to a high degree in weight fineness or immaturity, or, in other words, in Micronaire index. In that matter the quick and stable measurement of the Micronaire can give and has rendered a good service in production control [4].

(*4*) The fact that some fine cottons are much preferred in the cotton trade, although the fiber probably presents a small degree of maturity, depends on the end-use products. As is known, most correlation studies have shown that fiber fineness and, indirectly, low maturity are of high relative importance in obtaining a stronger yarn. It is not self-evident that a low maturity necessarily gives trouble from the standpoint of neppiness. The neppiness of a cotton depends on a combination of fiber properties among which the maturity is only of secondary importance.

(*5*) The meaning of the relationship found in Figure 3 which represent the Causticaire fineness plotted against Micronaire index-curvilinear scale is as follows:

The formula which gives the Causticaire fineness has been established in such a way that it takes into account the above considerations with a certain degree of precision. Fineness if plotted in a graph as a function of a linear Micronaire scale (the Causticaire scale is also approximately linear) should give parabolas with constant maturities. Because in the figure the data are plotted against a curvilinear scale, the parabolas change into straight lines. The line of 76% Causticaire maturity is one of those lines. The argument applies for readings made on raw cotton because there is a high linear correlation between readings on the Causticaire scale for mercerized fibers (T) and readings on the linear Micronaire scale for raw cotton fibers. The thing that makes the relation not rigorous is the difference in mercerizing ability between varieties. These differences exist but are practically negligible for normal cottons.

Concerning the Causticaire method for testing comber waste, we do not have much experience.

It is known that within a cotton variety the fibers are finer when the length is increasing, as is shown, for instance, in reference [2]. The variation in fineness as a function of fiber array length class is, moreover, characteristic for a certain variety. There are cottons with approximately constant fineness and others with marked differences in fineness between long and short length classes.

We suppose that, in a certain way, processing operations on cotton fibers break more of the fine ones and, of course, the immature fibers which are afterwards discarded on the comber. The fibers tested after combing could sometimes give a lower reading on comber waste than on the sliver.

In making sorter arrays it is stated that the hypothesis of constant fineness, if only for practical reasons, is held to simplify considerably the test procedure and calculations.

Literature Cited

1. Burley, S. T., Jr., and Bartness, E. S., The Causticaire Method for Determining Cotton Fiber Maturity and Fineness, Preliminary Report, U. S. Dept. Agr. (Aug. 1952).
2. De Meulemeester, D., and Raes, G., Caractéristiques de certaines variétés de coton spécialement congolaises, *I.N.E.A.C. Serie Technique*, Nos. 34 and 35 (1947).
3. De Meulemeester, D., Tison, L., Fransen, T., and Raes, G., La mesure de la perméabilité d'un échantillon de coton et son rapport avec la finesse gravimétrique et la maturité, Congrès international des sciences appliquées à l'industrie textile, **T28** (1951).
4. Regnery, W., Blending of Cotton by Fineness Determination and Other Application of Research in Mill Operation, TEXTILE RESEARCH JOURNAL **21** (1952).
5. U. S. Dept. Agr., Micronaire Fiber Fineness Scale for Use in Testing American Egyptian Cotton (Jan. 1952).

G. RAES
T. FRANSEN

The Nature of Fiber Friction

SWEDISH INSTITUTE FOR TEXTILE RESEARCH
Gothenberg, Sweden
July 23, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent paper, "Measurement of Friction between Single Fibers, Part VII: Physicochemical Views of Interfiber Friction," by Gralén, Olofsson, and Lindberg [1], the following equations were given for the frictional force between two fibers in the twist friction meter:

$$F = \alpha W + \beta lR; \tag{1}$$

$$F = \gamma\sqrt{WlR}. \tag{2}$$

Here F = frictional force, W = load, l = length of the contact line between the fibers, R = radius of the fibers, and α, β, and γ are constants. Equation (1) is valid for a deformation of a partly plastic, partly elastic type, and (2) is valid for a deformation of a wholly elastic type. The results considered in [1] are very well described by equation (1). However, later work by Howell *et al.* [2] and Lincoln [3, 4] has shown that the frictional forces for textile materials may be explained by considering the deformations to be of a wholly elastic character. For large values of W a plastic deformation may occur (experiments are not decisive), but for small values of W the deformation should be elastic, as the theory in [1] also indicates. This raises the question whether equation (2) is also comparable with the experimental results in [1]. If so, there should be some transition region where for decreasing W we pass from a relation of type (1) to a relation of type (2).

If we assume the transition to occur at some point P we should have

$$F_P = \alpha W_P + \beta(lR)_P = \gamma\sqrt{W_P(lR)_P} \tag{3}$$

To make the transition as smooth as possible we could also give the conditions for equality of the derivatives

$$\left(\frac{\delta F}{\delta W}\right)_P = \alpha = \frac{\gamma}{2}\sqrt{\frac{(lR)_P}{W_P}} \tag{4}$$

and

$$\left(\frac{\delta F}{\delta(lR)}\right)_P = \beta = \frac{\gamma}{2}\sqrt{\frac{W_P}{(lR)_P}}. \tag{5}$$

It is easily shown that one of the three equations (3), (4), and (5) may be derived from the other two, and calculations also give the identity

$$4\alpha\beta = \gamma^2. \tag{6}$$

If α, β, and γ are substituted into equation (6) from equations (15) and (17) in [1] we get the relation

$$4\alpha\beta/\gamma^2 = \pi(1 - \pi/4) = 0.67. \tag{7}$$

The circumstance that this ratio $\neq 1$ signifies that there is a "knee" in the F–W curve at P. We may choose some value for $(lR)_P$ and calculate the corresponding value of W_P, using (3), (4), or (5), the constants α, β, γ being given. In Figure 1 curves are drawn for nylon, the constants, taken from [1], being $\alpha = 0.257$, $\beta = 367$ (Table I of [1]); further, $E = 3\cdot10^7$; and [from (15) and (17)] $\gamma = 23.64$. As the range of (lR) is $2.5 - 8.0\cdot10^{-4}$, curves are given for $(lR)_P$ corresponding to these extreme values.

Now most experimental values in [1] correspond to W values to the right of or inside the transition re-

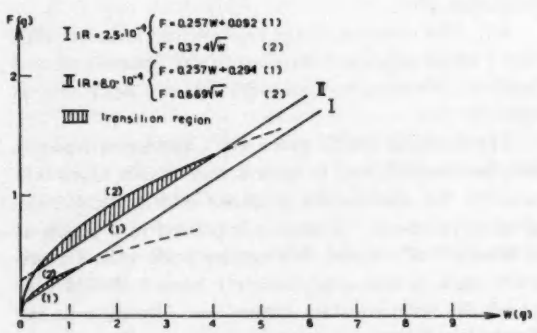

FIG. 1. *F-W curves for nylon from experimental results in [1].*

gion, and because of the smooth transition and the experimental error it is not possible to decide between curves 1 and 2 in this region. In [1] we have no values to the left of this region, but such measurements are given in [2] and [3]. However, as the real contact area is not known in [1], we cannot make a direct comparison of the results. The decision between the elastic and elastic-plastic type of deformation is further obscured by (*1*) the continuous transition between these states for fibers (cf. [2]); (*2*) the difference between the frictional relationship for a point contact and a real surface contact (cf. [4]). But all experiments justify the opinion that the mechanism of fiber friction is a shearing at the contact surfaces, the frictional force being proportional to the surface area, and this area being determined by the viscoelastic properties of the fibers.

Literature Cited

1. Gralén, N., Olofsson, B., and Lindberg, J., TEXTILE RESEARCH JOURNAL **23**, 623 (1953).
2. Howell, H. G., and Mazur, J., *J. Textile Inst.* **44**, T59 (1953).
3. Lincoln, B., *Brit. J. Appl.* **3**, 260 (1952).
4. Lincoln. B., *J. Textile Inst.* **45**, T92 (1954).

BERTIL OLOFSSON

An Orientation Concerning the Relations between Fiber and Yarn Properties in Several Mills

FIBER RESEARCH INSTITUTE T.N.O. OF THE NATIONAL COUNCIL FOR INDUSTRIAL RESEARCH
Enschede, The Netherlands
July 30, 1954

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The studies of the U. S. Department of Agriculture on the relations between fiber and yarn properties met with considerable interest in The Netherlands. It was realized, however, that Webb's multiple-regression equations for lea strength give much higher figures than those obtained in actual mill practice, and that in each mill a different set of relations will hold.

Eight mills were sufficiently interested to participate in an orientation study. The question was to what extent it would be possible, in actual practice, to control lea strength and other yarn properties by controlling cotton fiber properties.

Each mill took from its own stock 20 bales widely varying in type and origin and converted each cotton separately into warp yarns Ne 12, 16, 24, 36, and 50 (if possible), using its ordinary production line and settings. All testing was centralized in this laboratory. A summary * of some of the results may be of interest.

Mean Results of the Twenty Spinning Tests in Each Mill

The considerable differences between the mills in the *mean* results of the twenty spinning tests may be attributed mainly to differences in spinning technique since both the mean and the range of the cotton properties did not vary much from mill to mill.

Striking differences were observed in connection with neps. Neps were counted in raw cotton as well as in card webs. The mean percentage of neps retained in card web, calculated on the number of neps in raw cotton, did vary among the mills from 36% to 108%. This was, of course, reflected in yarn appearance (Ne 24): best mean B+, lowest mean C+. Other results for Ne 24 are: lea strength (pounds): highest mean 83, lowest 68; single-strand tensile strength (grams): highest mean 329, lowest 278; elongation at break (%): highest mean 8.7, lowest 7.3.

* A more complete report will appear in the September issue of the Dutch textile journal *De Tex* (in English); reprints may be had from the Fiber Research Institute.

Simple Correlations between Fiber Properties

The total number of cottons was 145. Several correlations reached the 5% significance level, but the only correlation of technological significance is between Micronaire reading and number of neps in raw cotton, this being −0.67.

Simple Correlations between Fiber and Yarn Properties

These correlations have been calculated for each yarn size and each mill separately; the frequency by which the 5% significance level was reached, summarizing all mills and all yarn sizes, is given in Table I.

Multiple Regression

In working out multiple correlations the bunch-analysis method of Frisch was used. Frequently, by this method, one or more fiber properties had to be rejected as a detrimental variable, resulting in simpler regression equations, which often were more in accord with technological experience.

The regression of neps in raw cotton on Micronaire reading could not be improved by introducing other variables.

For *lea strength*, 28 multiple-regression equations were worked out for each mill and each yarn size separately. In three of these equations four variables gave the best results (upper-half mean, uniformity, Micronaire reading, and Pressley index); in all other instances a smaller number of variables led to a more suitable regression equation. The share of upper-half mean in the multiple correlation was highest nineteen times, Pressley index was highest eight times, and uniformity once. The multiple correlation coefficients run from 0.932 to 0.677; random variations, not explainable by variation in cotton properties, consequently run from 13 to 54%.

By substituting the fiber properties of a "hypothetical" cotton in all the regression equations, a comparison of the ability of the mills in obtaining lea strength is obtained. Calculating the mean of the predictions for five hypothetical cottons, in each mill, the lowest mean is only 76% of the highest. The regression equations indicate also that a considerable "loss" in lea strength occurs in some mills.

Multiple-regression equations were calculated for other yarn properties, but for one mill only, a mill which had a high multiple correlation for lea strength.

The multiple correlation coefficients for *single-strand tensile strength* were slightly higher than for lea strength (on the same variables: upper-half mean, uniformity, Micronaire reading, and Pressley index): for Ne 16, 0.95 against 0.93; for Ne 24, 0.91 against 0.88.

The best set of variables explaining *elongation at break* were upper-half mean and Pressley index, leading to multiple correlation coefficients for Ne 16 to 0.72 and for Ne 24 to 0.70.

The single regressions for neps in card web on Micronaire reading, for yarn appearance on neps in card web, for yarn modulus on Pressley index, and for Uster irregularity on upper half mean could not be improved by introducing other variables.

Most of the practical value of this study has been on sidelines or indirectly. It has stimulated attention toward fiber properties in connection with spinning properties (neps) and yarn quality; it has stimulated improvements in processing in several mills.

TABLE I. SIMPLE CORRELATIONS BETWEEN FIBER AND YARN PROPERTIES; FREQUENCY OF CORRELATION COEFFICIENT REACHING THE 5% LEVEL

	Yarn appearance	Lea strength	Elongation at break	Uster irregularity
Upper-half mean length	1+	21+	7+	8−
Uniformity	4+	6+	0	3−
Pressley strength	0	13+	14−	0
Micronaire reading	14+	5−	5−	3−; 1+
Maturity	2+	0	0	0
Neps in raw cotton	21−	—	—	6+
Neps in card web	20−	2+; 3−	—	8+; 2−
Number of corr. coeff.	28	28	28	28

+ = positive correlation; − = negative correlation.

Acknowledgment

The writers would like to express their appreciation for the permission to publish these data given by the directors of the mills participating in this research project. The interest and the suggestions of the Director of the Fiber Research Institute T.N.O., Ir J. R. H. Van Nouhuys, and of Mr. T. J. D. Erlee, Head of the Statistical Department, T.N.O., were very stimulating.

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The Dyeing of Cyanoethylated Cotton

Southern Regional Research Laboratory
Southern Utilization Research Branch
Agricultural Research Service
New Orleans, Louisiana
June 7, 1954

To the Editor:
Textile Research Journal

Dear Sir:

The current interest in cyanoethylated cotton stimulated by Compton [4, 5], has been concentrated on the heat and rot resistance of this modified cotton. Compton has claimed that cyanoethylated cotton was more receptive than cotton to all classes of dyestuffs.

We have found that, in general, methods employed in the dyeing of polyacrylonitrile fibers, such as Dynel* and Orlon,*† can be applied to cyanoethylated cotton of low substitution; and basic dyes such as du Pont's Basic Blue OB,* Basic Red 4G,* and Basic Yellow OL,* which do not ordinarily dye cotton, will dye cyanoethylated cotton. Successful applications have been made from a 2 to 3% dye bath containing sodium acetate and acetic acid, as recommended by Crawford [6]. The weight of dye was based on the weight of the cyanoethylated cotton, and the bath contained 50 g. of water per gram of cotton. Although only a slight amount of color is obtained on cotton containing 1 cyanoethyl group for every 4 anhydroglucose units of the cellulose (2.0% N), extremely bright shades are obtained when the substitution is equivalent to 1 cyanoethyl group for every 2 anhydroglucose units (4.0% N).

More impressive results are obtained with acid dyes, using the cuprous-ion method of Feild and Fremon [7], modified by Blaker [1, 2, 3], with the technique recommended by Crawford [6]. Dyes employed were Fast Red S Conc.* (C.I. 176 National Aniline), Anthraquinone Blue BN* (C.I. 1054 du Pont), and Orange II* (C.I. 151 Eastman Kodak Company #196).

These dyes cause only a slight discoloration of untreated cotton, which is increased to an extremely light shade by the presence of cyanoethyl groups. In other words, these acid dyes are absorbed to only a negligible extent by cyanoethylated cotton with substitutions as high as 1 cyanoethyl group per anhydroglucose unit (6.5% N).

With 2% dye in the presence of 3% copper sulfate and 1.5% hydroxylamine sulfate as a reducing agent, perceptible dyeing is obtained with cyanoethylated cotton containing as little as 0.5% N, or 1 cyanoethyl group for every 17 anhydroglucose units of the cellulose. Extremely dark shades result with cyanoethylated cotton containing 2.0% N or higher. A lower dyeing capacity was observed with substitutions higher than 2 cyanoethyl groups per glucose unit.

* The mention of trade names does not imply endorsement by the Department of Agriculture over similar products.
† Acrylic fiber, Du Pont.

Literature Cited

1. Blaker, R. H., U. S. Patent 2,653,074.
2. Blaker, R. H., Katz, S. M., Laucius, J. F., Remington, W. R., and Schroeder, H. E., *Disc. Faraday Soc.*, No. 16, 210–222 (1954).
3. Blaker, R. H., and Laucius, J. F., *Am. Dyestuff Reptr.* **41**, P39–43 (1952).
4. Compton, J., *Am. Dyestuff Reptr.* **43**, P103–111 (1954).
5. Compton, J., *Textile Inds.* **117**, 138A–138D, 188 (1953).
6. Crawford, D. J., *Can. Textile J.* **71**, 61–70 (1954).
7. Feild, T. A., and Fremon, G. H., Textile Research Journal **21**, 531–539 (1951).

H. A. Schuyten
J. W. Weaver

INDUSTRIAL SECTION

The Influence of Friction and Traveller Weight in Ring Spinning

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Introduction

In previous papers [1, 2] the authors examined the way that the shape and tension of the ballooning thread in a cap-spinning system are influenced by technical features such as the dimensions of the spinning frame and the properties of the yarn. The present paper describes similar work on a ring-spinning system. The variables examined are traveller weight, friction between the traveller and the ring, friction between the traveller and the yarn, and bobbin speed. The method of calculation is the same as that used previously, *i.e.*, solutions of the equations of motion of the ballooning thread are first obtained using the differential analyzer, and then the solution which applies to a given set of spinning conditions is selected by considering the forces acting on the traveller. These forces are discussed below. The forces assumed to act on an element of ballooning thread, the equations of motion, and the method of solution are precisely the same as those discussed in the earlier papers. In particular, the air drag on a given element of thread is assumed to be proportional to the square of the wind velocity and to act normally to the element.

Spinning Conditions

The calculations refer to an idealized system. The basic dimensions and speeds are taken to be those given in Table I, and the yarn is assumed to be in the form of a single thread of uniform circular cross section, perfectly flexible and inextensible.

Equations of the Ballooning Thread

With reference to axes OX, OY, and OZ rotating about OZ with the constant angular velocity ω of the ballooning thread, the equations of motion of an element of thread in the balloon are taken to be:

$$\frac{d}{ds}\left(T_z\frac{dx}{ds}\right)+\frac{fy}{r}\cos^3\theta+2mv\omega\frac{dy}{ds}+m\omega^2x=0, \quad (1)$$

and

$$\frac{d}{ds}\left(T_z\frac{dy}{ds}\right)-\frac{fx}{r}\cos^3\theta-2mv\omega\frac{dx}{ds}+m\omega^2y=0. \quad (2)$$

Here s is the distance along the thread and T_z is the vertical component of a modified thread tension, $T-mv^2$, where T is the true tension in grams. Other nomenclature is as given in Table I. If gravity and the small vertical component of air drag are neglected, T_z is constant. The full derivation of equations (1) and (2) is given in the previous papers [1, 2].

Forces on the Traveller

The forces acting on the traveller are its weight, thread tensions, the reaction of the ring, and the frictional force between the traveller and the ring. These forces are shown in Figure 1. Here P is the tension in the yarn between the traveller and the

TABLE I

Height of balloon (h)	30.48 cm. (12 in.)
Radius of ring (R)	6.98 cm. (2.75 in.)
Radius of bobbin (b)	3.49 cm. (1.375 in.)
Spindle speed (N)	125 r.p.s. (7500 r.p.m.)
Spinning speed* (v)	375 cm./sec. (12.3 ft./sec.)
Speed of revolution of balloon ($\omega/2\pi$)	107.91 r.p.s. (6475 r.p.m.)
Mass of yarn per unit length (m)	1.555×10^{-4} g./cm. (140 den.)
Diameter of hypothetical yarn	0.0112 cm. (0.0045 in.)
Traveller weight (M)	0.0403 g.

* The speed at which the yarn enters the top guide.

bobbin (in future referred to as "bobbin tension"), T is the tension in the yarn just before it passes under the traveller, R_H and R_V are the horizontal and vertical components of the reaction of the ring on the traveller, F is the frictional drag of the ring on the traveller, M is the traveller weight, ω is its angular velocity; and R is the radius of the ring. The angles θ and ϕ were introduced previously [1, 2]. θ is the lean-back angle given by $\cos\theta = ds_1/ds$, where ds is an element of ballooning thread and ds_1 is its projection on the meridian plane, *i.e.*, the plane containing the axis of the balloon and the radius r to the element; θ_o is the lean-back angle at the traveller. ϕ is the angle given by $\sin\phi = dr/ds$, and ϕ_o is its value at the traveller. Resolving along the radius gives

$$P\cos\alpha + T\cos\theta_o\sin\phi_o - R_H = MR\omega^2, \quad (3)$$

and along the tangent to the traveller motion

$$P\sin\alpha = F + T\sin\theta_o. \quad (4)$$

Resolving vertically gives

$$R_V + Mg = T\cos\theta_o\cos\phi_o. \quad (5)$$

The resultant reaction between ring and traveller is $(R_H^2 + R_V^2)^{\frac{1}{2}}$; hence the frictional force F is given by

$$F = \mu_1(R_H^2 + R_V^2)^{\frac{1}{2}}, \quad (6)$$

where μ_1 is the coefficient of friction between ring and traveller. Substituting for R_H and R_V from equations (3) and (5) and then for F in equation (4) yields

$$P\sin\alpha = T\sin\theta_o + \mu_1[(T_z - Mg)^2 + (P\cos\alpha + T\cos\theta_o\sin\theta_o - MR\omega^2)^2]^{\frac{1}{2}}, \quad (7)$$

where $T_z = T\cos\theta_o\cos\phi_o$ is the vertical component of tension at the traveller. Because the thread is running through the traveller, the bobbin tension P exceeds T, and we shall assume that

$$P = T\exp(\mu_2\pi/2), \quad (8)$$

where μ_2 is the coefficient of friction between yarn and traveller. We make this simplifying assumption because we do not know, in general, exactly how the yarn passes through the traveller nor at what angle the traveller sets itself across the ring under the action of the various forces. This assumption seems unlikely to lead to serious errors for the angles involved in practice, and it allows general results to be obtained without too much complication of the mathematics. Of the solutions of the equations of motion of the ballooning thread obtained by the differential analyzer, the one for which equation (7) is satisfied gives the balloon shape and bobbin tension for the particular spinning conditions under consideration. In addition to the variables specified in Table I, these conditions include the coefficients of friction μ_1 and μ_2. If each side of equation (7) is plotted against the vertical component of tension, T_z, for each solution calculated by the differential analyzer, the intersection of the two curves gives the value of T_z required. The corresponding bobbin tension and balloon shape can then be deduced by interpolation on the family of calculated solutions.

An alternative procedure which can be used to study the effect of μ_1, for example, and which is more economical of basic solutions, is to solve

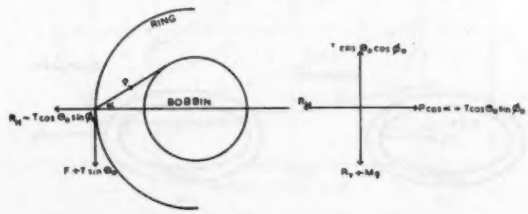

FIG. 1. *Forces on the traveller.*

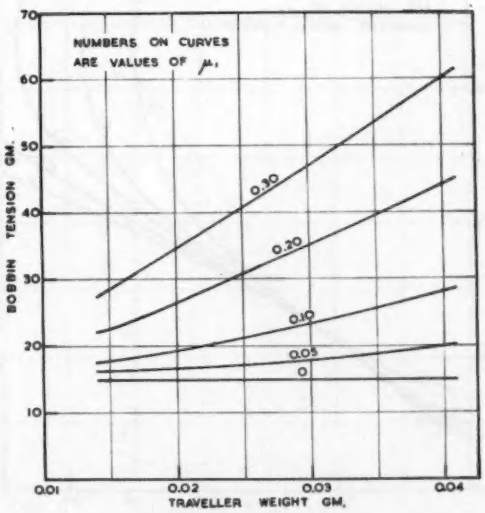

FIG. 2. *Effect of traveller weight for a smooth yarn.*

equation (7) for μ_1; *i.e.*,

$$\mu_1 = \frac{T\,[\exp(\mu_2\pi/2)\sin\alpha - \sin\theta_o]}{[(T_z - Mg)^2 + (P\cos\alpha + T\cos\theta_o\sin\phi_o - MR\omega^2)^2]^{\frac{1}{2}}}. \quad (9)$$

By evaluating a number of solutions for chosen values of T_z and substituting the values of T, P, θ_o, etc., so obtained into equation (9), the value of μ_1 to which the solution corresponds can be deduced.

Calculated Results

Traveller Weight

Figure 2 shows how bobbin tension depends on traveller weight when the coefficient of friction between the yarn and the traveller is taken to be zero. If the ring is perfectly smooth ($\mu_1 = 0$), bobbin tension is independent of traveller weight. Otherwise, tension increases approximately linearly with increasing traveller weight, the increase being more marked the greater μ_1 is. Results for other values of μ_2 are essentially the same as those shown in Figure 2 as far as general behavior is concerned.

Friction

Figure 3 shows, for a traveller weight of 0.0403 g., how bobbin tension depends on the two coefficients of friction μ_1 and μ_2. Clearly, there is a wide range in μ_1 over which μ_2 has relatively little effect.

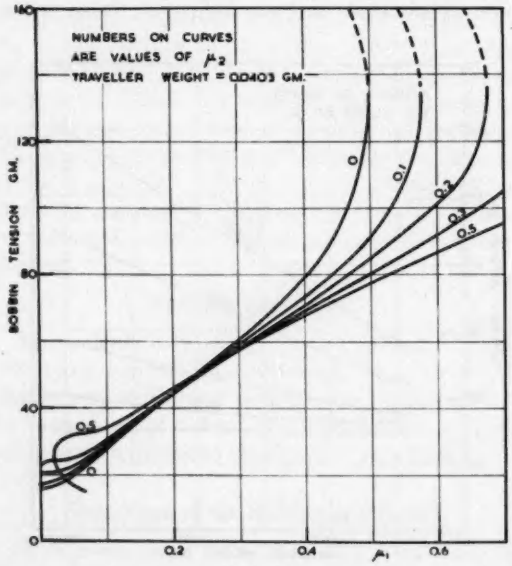

FIG. 3. *Effect of friction.*

For any value of μ_2 there is an upper limiting value of μ_1 beyond which no balloons exist; *i.e.*, if the coefficient of friction between the ring and the traveller exceeds a certain value, spinning becomes impossible. The significance of this upper limiting value can be seen from equation (9). When numbers are substituted in the expression for μ_1, the term $(P\cos\alpha + T\cos\theta_o\sin\phi_o - MR\omega^2)$ in the denominator is found to pass from negative values through zero to positive values as T_z is increased. This means that the square of this term passes through a minimum value; hence μ_1 passes through a maximum value, as shown in Figure 3. Furthermore, it may be seen from equation (3) that this means that R_H, the horizontal component of the reaction between the ring and the traveller, is zero at the limiting value of μ_1. Along the lower parts of the curves of Figure 3, shown by solid lines, R_H is negative; that is to say, the traveller is pressing on the inner surface of the ring. Along the upper parts of the curves, shown dashed in Figure 3, R_H is positive and the traveller presses on the outer surface of the ring. At the upper limiting value of μ_1, the distribution of forces on the traveller changes from that of Figure 4a to that of 4b. When the yarn tension is low, it is incapable of overcoming the effect of centrifugal force, and the traveller is prevented from flying outwards by the reaction of the ring. For high tensions, on the other hand, the traveller would be pulled inwards were it not for the reaction of the ring.

The curve for $\mu_2 = 0.5$ in Figure 3 shows also a lower limiting value of μ_1. This has its origin in the existence of a maximum lean-back angle, θ_o, such as was discussed in the previous papers [1, 2] and as is shown in Figure 5, where $\sin\theta_o$ is plotted against $T_o = T_z g/mh^2\omega^2$. Here T_z is the vertical component of tension in grams. Referring again to equation (9), it is clear that, for low values of μ_2, $\sin\theta_0$ may become equal to $\exp(\mu_2\pi/2)\sin\alpha$; hence

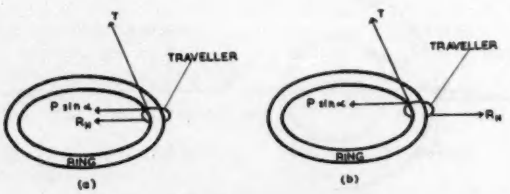

FIG. 4. *Forces on the traveller.*

μ_1 becomes zero, as is so for $\mu_2 = 0, 0.1, 0.2, 0.3$ in Figure 3. For $\mu_2 = 0.5$, however, even the maximum value of $\sin\theta_o$ in Figure 5 ($\sin\theta_o = 0.84$) is less than $\exp(\mu_2\pi/2)\sin\alpha$ and μ_1 is never zero. Instead, there is a lower limit to the value of μ_1, as shown by the curve for $\mu_2 = 0.5$ in Figure 3, below which no balloons are possible.

Bobbin Speed

The influence of bobbin speed is shown in Figure 6 for the traveller of weight 0.0403 g., assuming no friction between the yarn and the traveller. By examining equations (1), (2), and (7) when written in nondimensional variables, as in the Appendix of [1], it can be seen that bobbin tension in grams is very nearly proportional to ω^2, where ω is the angular velocity of the traveller. The curves of Figure 6 are plotted by using this fact and the equation connecting ω with spindle speed N; *i.e.*,

$$2\pi N = \omega + v/b. \tag{10}$$

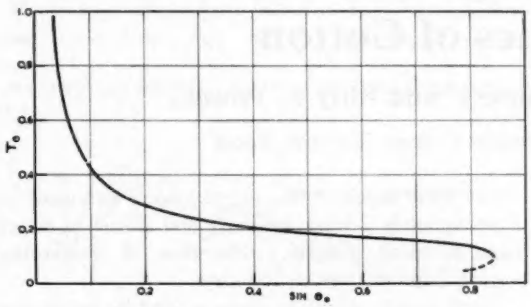

FIG. 5. *Effect of T_o on $\sin\theta_o$.*

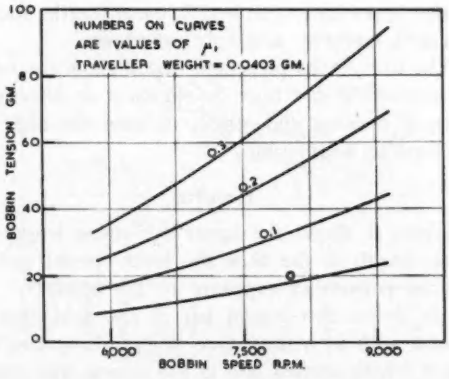

FIG. 6. *Effect of bobbin speed for a smooth yarn.*

It follows that the general effect of changing spindle speed is always as in Figure 6, whatever the traveller weight and the coefficients of friction.

Balloon Profiles

The profile of the balloon is determined by the parameter $T_o = T_z g/mh^2\omega^2$ (see the Appendix of [1]), provided that we confine attention to one yarn. Here T_z is the vertical component of tension in grams, assumed constant throughout the balloon, and m, h, and ω are defined as in Table I. It follows, therefore, that the balloon profiles drawn in Figure 7 for the two different values of T_o, 0.88 and 0.40, can be associated with any set of conditions which gives rise to these values. The calculated results show that $T_o = 0.40$ when $M = 0.014$ g., and $T_o = 0.88$ when $M = 0.0403$ g., if $\mu_1 = 0.3$ and $\mu_2 = 0$ in each case. Thus for these coefficients of friction the larger balloon of Figure 7 is obtained by using the lighter traveller, and the narrower balloon by using the heavier traveller. Alternatively, if we restrict ourselves to the heavier traveller and a smooth yarn ($\mu_2 = 0$), the balloon grows from the smaller one to the large one shown in Figure 7 as μ_1 is decreased from 0.3 to 0.1. A "licking" balloon would be produced by a T_o value of about 0.1, corresponding, for example, to a traveller weight of 0.0403 g. when $\mu_1 = 0.02$ and $\mu_2 = 0.5$. This is the lower limiting value of μ_1 in Figure 3.

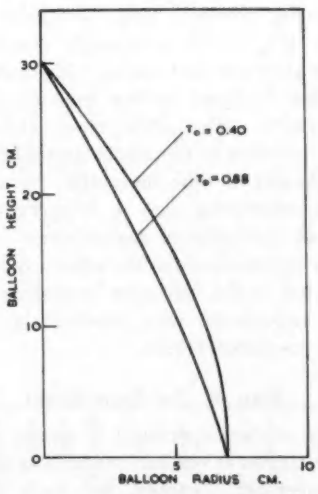

FIG. 7. *Balloon profiles.*

Summary

The influence of a number of factors on the behavior of a ring-spinning system has been investigated theoretically. The factors are traveller weight, the coefficients of friction between the ring and the traveller and between the yarn and the traveller, and bobbin speed. Bobbin tension always increases with increasing traveller weight, and usually also with increasing coefficient of friction between the ring and the traveller. Variations of friction between the yarn and the traveller are less important in the range corresponding to practical conditions. There is an upper limit to the coefficient of friction between the ring and the traveller above which spinning appears to be impossible. Also, for the higher values of the coefficient of friction between the yarn and the traveller, it is necessary for the frictional coefficient between the ring and the traveller to exceed a certain value. Provided that the yarn is not too rough, *i.e.*, the coefficient of friction is less than 0.5, however, spinning is possible even with a perfectly smooth ring. The calculated results are obtained for one particular spinning system, but the general conclusions should hold for other systems.

Literature Cited

1. Crank, J., and Whitmore, D. D., TEXTILE RESEARCH JOURNAL **23**, 657 (1953).
2. Crank, J., and Whitmore, D. D., TEXTILE RESEARCH JOURNAL **24**, 434 (1954).

(Manuscript received June 21, 1954.)

The Effect of Weathering in the Field on the Fiber Properties of Cotton

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THIS paper is concerned with what happens to cotton from the time the boll opens until the cotton is ginned. Considerable research has been done on the effects of biological decay produced by microorganisms [7], which is brought about by damp conditions after the boll opens. Biological decay is more or less localized by dew and rain during the picking period. The other types of weathering, which are common to the whole cotton belt and vary with the length of time the cotton remains on the plant, are weathering due to temperature change, drying, and oxidation of the cellulose by sunlight. To obtain information on the effects of weathering on cotton left in the field over increasing periods of time, an experiment was planned the results of which are presented herein.

Plan of the Experiment

The plan of the experiment is shown in Table I. Bolls were tagged at regular intervals as they opened during September, October, and early November. From these tagged bolls, samples were harvested at approximately 2-week intervals and stored in paper bags to await ginning. The time of weathering varied from 11 days to 153 days.

Each sample was fully characterized by measuring the physical properties of the fiber to determine the weathering effect. The properties measured included upper-half mean length, mean length, fineness, strength, maturity, and light reflectance.

The five graphs presented herein show the results of weathering and fiber development as affected by time of opening and length of time the fiber was exposed to weathering.

Results

Figure 1 shows the upper-half mean length and mean length at the time the bolls opened and for various periods of exposure to the weather. The graph shows that cotton left in the field gins out shorter with increasing time of exposure; also, that cotton which opened late in the season was shorter due to underdevelopment brought about by greater shrinkage from immature fiber.

* Fiber and Spinning Laboratory of The Cotton Research Committee of Texas.

Figure 2 shows the fiber fineness as measured by the Micronaire. No effect on fineness was evident from weathering in the field; however, the results of underdevelopment were plainly evident in late-opened cotton.

There is no reason why maturity should be affected by weathering to a greater degree than fineness, since maturity and fineness are correlated within varieties. Figure 3 shows less maturity for the cotton that opened late in the season.

TABLE I. PLAN OF WEATHERING TEST EXPERIMENT—YEAR 1953

Date bolls harvested	Date bolls tagged* Sept. 4	Sept. 15	Sept. 28	Oct. 12	Oct. 26	Nov. 9
Sept. 4	X					
15	X	X				
28	X	X	X			
Oct. 12	X	X	X	X		
26	X	X	X	X	X	
Nov. 9	X	X	X	X	X	X
27	X	X	X	X	X	X
Dec. 11	X	X	X	X	X	X
28	X	X	X	X	X	X
Jan. 15	X	X	X	X	X	X
Feb. 1	X	X	X	X	X	X

* *Cracked* and *fully* open bolls were gathered at the tagged date.

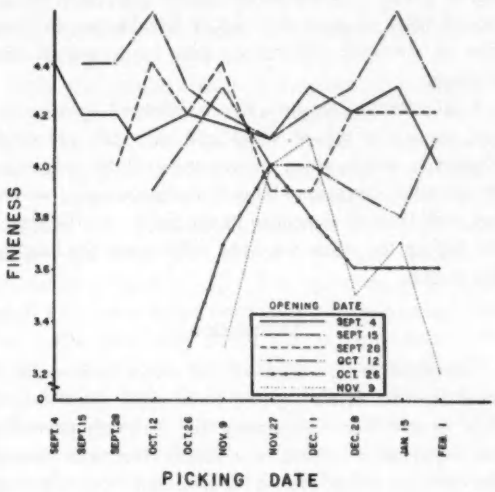

FIG. 2. *The effects of weathering and time of boll opening on fiber fineness.*

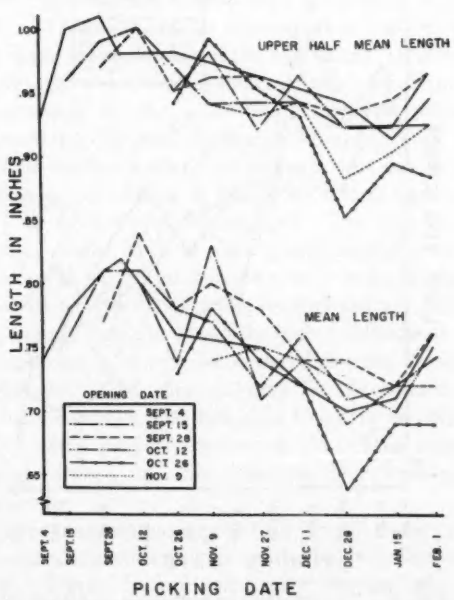

FIG. 1. *The effects of weathering and time of boll opening on fiber length.*

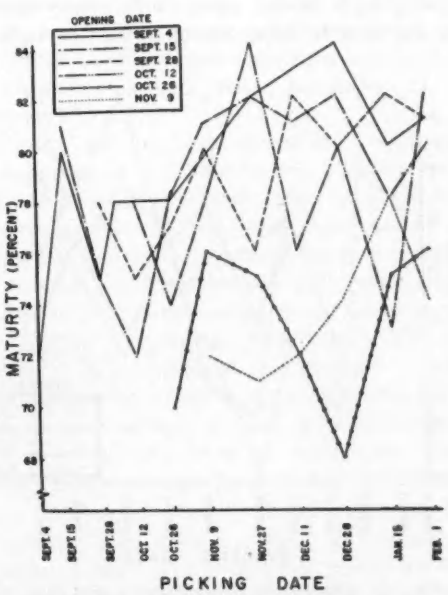

FIG. 3. *The effects of weathering and time of boll opening on fiber maturity.*

Figure 4 indicates how the fiber strength of cotton, as measured by the Pressley instrument, was affected by exposure to weathering in the field. There was no evidence of loss of strength as measured by the zero-gauge Pressley determination. The strongest cottons were the two latest, or those that had the finest fibers. Since more fibers per unit weight would tend to give the higher breaks, an explanation of strength differences may be found in fiber fineness.

Undoubtedly, cotton color is affected by weathering, especially where wind and rain are prevalent. Figure 5, which gives a measure of light reflectance or cotton brightness, showed increased color of cotton with time of exposure in the field. In the graph, the higher the value for light reflectance the brighter the cotton.

Discussion

The weathering effects in this experiment must be attributed to factors other than rain, since only a little over 0.2 in. fell during the 5-month period of the experiment. Just how much dew was present and what its effect would be is hard to say, although dew may be a factor. Alternate wetting and drying play a part in the degradation of cotton fiber. This is the process used in the dew retting of hemp fiber. Wetting and drying along with microorganisms free the fiber in hemp retting from the encrusting materials. In some respects the primary wall of cotton is comparable to the encrusting materials of hemp fiber, since a number of organic materials of lesser molecular weight than cellulose are present, and these components may be expected to respond more readily to the degradation brought about by wetting and drying. Furthermore, it is known that the cellulose of the primary wall is of a considerably lower degree of polymerization and may respond more readily to degradation from these forces of decomposition [5].

The changes in length shown in Figure 1 may occur for a number of reasons. Cotton which is allowed to ripen under exceedingly dry conditions can be expected to approach brittleness and the fiber would shatter on ginning in a dry state. In a close inspection of nep-producing fibers, the U. S. Department of Agriculture found that 14% of the fibers in neps were of the fragment type [1]. This laboratory has found that, when processing dry cotton through picking, a loss of 10% in yarn strength was experienced which may be partially attributed to shorter fiber produced through fragmentation. The fact that the mean length of the fibers shows a greater

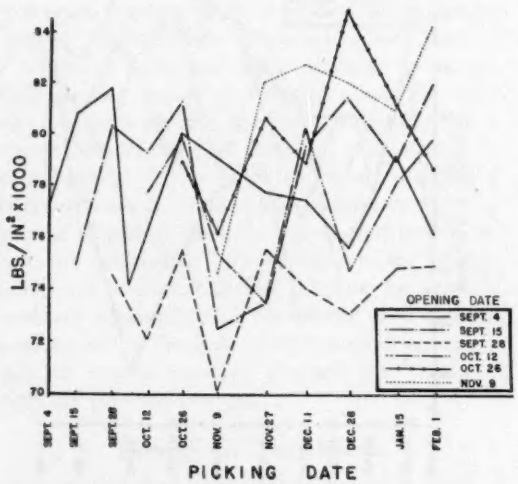

FIG. 4. *The effects of weathering and time of boll opening on fiber strength.*

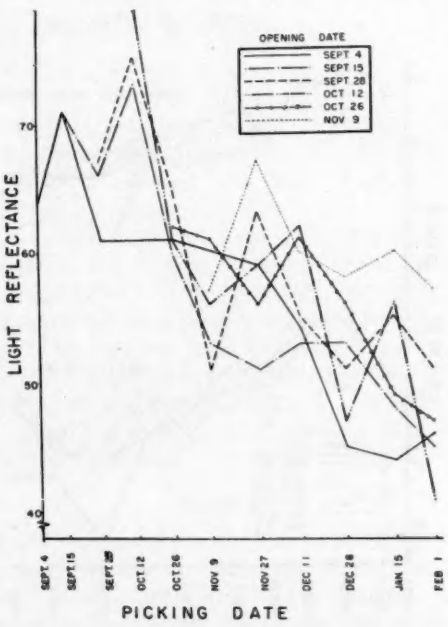

FIG. 5. *The effects of weathering and time of boll opening on fiber color.*

decrease in length than the staple length is further evidence of loss of fiber length through fiber damage.

Changes in the internal structure of cotton through drying may also be a factor in shortening the fiber. Cotton will gain length if the moisture of the fiber is increased from a dry state. Since cotton has a spiral structure, it contracts and expands to give changes in length with moisture. Drying over long periods may increase the amount of crystalline cellulose over the amorphous fraction and tend to make the retraction of the fiber more permanent, thus decreasing the fiber length.

Weathering was not expected to affect the fineness of cotton fiber. Figure 2 indicates a rather uniform range of fineness for the first three samples to open over the whole 5 months the cotton remained in the field. The samples that opened in October and November showed some of the irregularities of late cotton. These samples had variations of from 3.3 to 4.3 Micronaire units. Especially the last two samples to open showed the effects of underdevelopment in fiber properties. These samples lacked uniformity, and the results are evident from the graph.

Maturity should be expected to follow fineness in this experiment. The three late samples were variable over the weathering period and had the lowest maturities. The three samples that opened early showed an increase in maturity with time in the field. This is difficult to explain other than to say that possibly weathering in the field effects structural differences, which in turn indicate increased maturity as measured by the polarizing-microscope method of measuring the wall thickness of cotton.

There was no evidence of strength loss due to the weathering of cotton in the field, which was contrary to what might be expected. The use of the Pressley tester jaws at zero gauge would tend to mask weak spots in the fiber and make strength losses more difficult to detect by this method. Hidden damage brought about through oxidation of the cellulose chain cannot be detected by the Pressley instrument. This damage may be determined by viscosity methods, and has been found to be considerable when properly evaluated [5]. This type of damage shows up after finishing and subsequent laundering.

Other than decreasing the fiber length, the greatest damage to the cotton from weathering was increased color. Figure 5 shows that color damage was not severe until after at least 2 months of exposure; then light reflectance dropped sharply. Fortunately, graying, if caused by dirt or other contaminants, is not permanent, and responds readily to kiering and bleach to gain a whiteness equivalent to brighter cottons. However, this does not hold when color is due to biological degradation [3]. If sufficient moisture were present during exposure to weather, the color damage would be more of a problem because pigments produced by microorganisms are more difficult to remove.

Since the primary wall of a cotton fiber may act as a protective coating during exposure to weathering in the field, some thought should be given as to how the constituents of this wall may be affected. A typical primary wall may be composed of 54% cellulose, 14% protein-like material, 9% peptic substances, 8% wax, and 4% of a polysaccharide containing glucosamine [8]. The cellulose of the primary wall has a lower degree of polymerization than that of the main body of the fiber or secondary thickening, and is more easily degraded on drying than the cellulose from the secondary wall. In fact, the cellulose of the primary wall loses nearly half its degree of polymerization on normal drying which takes place on opening in the field [5]. From the data cited, several months in the field would have a highly degrading effect on the cellulose of the primary wall. Other materials of the primary wall would be degraded similarly. Marsh [6] has shown that the wax content of cotton increases under field weathering. This indicates that the wax is freed by degradation from some other constituent of the primary wall.

Although strength losses produced by weathering are negligible as measured by the Pressley tester, there is hidden damage which shows up in finishing the yarn and fabric. Subsequent laundering or any alkaline boil will break the oxygen bonds in the cellulose structure and thus produce weak points in the cellulose chain. Such damage is not great until a large number of bonds have been broken [2].

Whereas this experiment was designed to study cotton weathering in the field, it has substantiated some previous findings on fiber development as influenced by the time when the bolls open. Early opening has meant longer, coarser, and more mature cotton. It was observed in the present work that late opening gave stronger cotton. A possible explanation of this is that shortage of water may have produced stress on the plant, resulting in stronger cotton than the earlier-opened cotton, which was

developed under conditions of adequate moisture [4] Then, too, as mentioned under "Results," fineness may influence strength by giving more fibers per unit area.

Acknowledgment

This work was done in cooperation with the Texas Agricultural Experiment Station, Lubbock, Texas, under the direction of Mr. Don Jones. Appreciation is expressed to Mr. Levon Ray, agronomist of the station, for aid in planning the experiment and handling the sampling. Graphs were made by Mr. Frank Louis, Cotton Research.

Literature Cited

1. Carpenter, F., An Evaluation of Various Ratios for Classification of Cotton Fibers for Maturity, U. S. Dept. Agr., Cotton Branch, Production and Marketing Administration, March, 1953.
2. Conrad, C. M., Tripp, V. W., and Mares, T., TEXTILE RESEARCH JOURNAL **21**, 726 (1951).
3. Crawley, T. V., Towery, J. D., Power, B. K., and Hessler, L. E., *Textile World* **102**, 100 (1952).
4. Hessler, L. E., *Textile Ind.* **117**, 94 (1953).
5. Hessler, L. E., Merola, G. V., and Berkley, E. E., TEXTILE RESEARCH JOURNAL **18**, 628 (1948).
6. Marsh, P. B., Barker, H. D., Kerr, T., and Butler, M. L., TEXTILE RESEARCH JOURNAL **20**, 297 (1950).
7. Marsh, P. B., Guthrie, L. R., and Butler, M. L., TEXTILE RESEARCH JOURNAL **21**, 565 (1951).
8. Tripp, V. W., Moore, A. T., and Rollins, M. L., TEXTILE RESEARCH JOURNAL **21**, 886 (1951).

(*Manuscript received July 26, 1954.*)

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